THE CARBONISATION OF COAL

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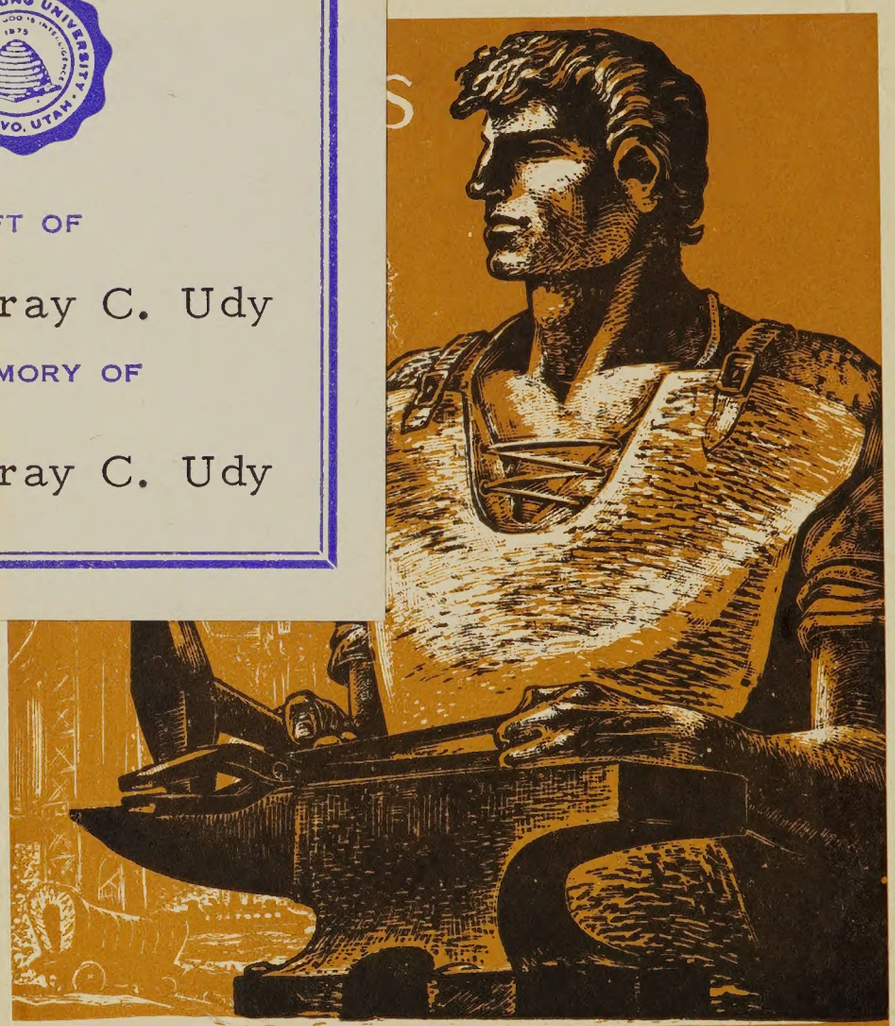

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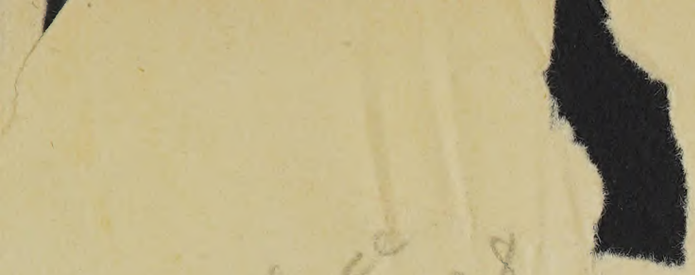

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THE CARBONISATION OF COAL

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THE CARBONISATION OF COAL

A SCIENTIFIC REVIEW OF THE FORMATION, COMPOSITION AND DESTRUCTIVE DISTILLATION OF COAL FOR GAS, COKE AND BY-PRODUCTS

BY

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INTRODUCTION

The Cantor Lectures which I gave in the winter of 1911 at the Royal Society of Arts, on the "Carbonisation of Coal," brought me so many letters of inquiry on various points connected with the subject that I thought it might be of interest to some at least of those engaged in carbonising work if I took the lectures as a basis for a short treatise on the subject, and I think the absence of any book dealing at all fully with the scientific side of carbonisation justifies the attempt. During the last forty years I have been interested in many fuel problems, and have had the good fortune during that period to assist at the birth of most of the new departures from the recognised rut of procedure, and also, I regret to say, have been a mourner at the funerals of many.

I have attempted to treat my subject in such a way as to awaken interest in many new points without burdening the reader with too much scientific detail, and although many of my views will not, I fear, be acceptable to all my readers, they will be recognised as an earnest attempt to present several subjects from a different point of view to that generally adopted.

The theory of the composition of coal which I have elaborated, and which in its crudest form dates back to the days when that giant amongst metallurgists, Dr Percy, ruled supreme at the Royal School of Mines in Jermyn Street, and which has again been brought to the front by recent investigations, is one that has never been developed fully; and one of the objects of this book is to show the way in

which it explains and fits in with most of the points which have proved difficulties in explaining many actions taking place during the destructive distillation of coal. At the same time, the last ten years have been marked by such wonderful activity in carbonising methods that there has been no lack of material to draw upon in trying to define the probable lines along which future advances will be made ; and I desire to express my indebtedness to the *Journal of the Society of Chemical Industry*, the *Gas World*, and the *Journal of Gas Lighting*, from the pages of which the student can glean every detail of the advances in carbonisation that will make the early years of this century as remarkable in the annals of the gas industry as was the corresponding period of the last century.

Greenwich, 1912.

CONTENTS

INTRODUCTION . . . . . *p.* v

CHAPTER I

THE FORMATION AND COMPOSITION OF COAL

Primary source of energy—The atmosphere of prehistoric days—Formation of carbon dioxide during combustion, respiration and fermentation—Decomposition of carbon dioxide by vegetation—The action of chlorophyll—Calories and British Thermal Units—Formation of vegetable deposits in the carboniferous period—Drift deposits—Action of time, temperature and pressure—Conversion of woody fibre to coal—Theories as to the nature of the change—Mineral constituents in coal—Nitrogen—Water—Cellulose and ligno-cellulose—Humic and ulmic acids—Tertiary coals, brown coals and lignites—Resin constituents—Formation of boghead cannel and shale—Theory of the constitution of coal—The binding material in coke—Weathering of coal—Spontaneous ignition—Pyrites—Ignition point of coals—Absorptive power of coals—Action of solvents on coal—Anilin and pyridine—Extraction of coal by pyridine—Water in coal—Ash of coal—Gruner's classification of coal—microscopic character of coal . . . . . *pp.* 1–38

CHAPTER II

THE CLASSIFICATION AND DISTRIBUTION OF COAL

Bituminous coal—Brown coals and lignites—Classification of coals by chemical composition—Proposed classifications of Fleck, Hilt and Parr—Gruner—Seyler's tabulation—Diagrammatic representation of the formation of coal—Ratio of the constituents of coal—Composition of peat and lignites—Calorific value of coal and coal constituents—Practical application to theory—Calorific value of humus—Work of Brame and Cowan and Constam and Kolbe on the calorific value of coals—The English coal-fields and their characteristics—Coal capital and production—Percentage of coal utilised for various purposes—Possible economies in coal consumption . . *pp.* 39–63

CHAPTER III

THE FORM OF RETORTS USED IN GAS MANUFACTURE

The early work of Murdoch—Apparatus for the distillation of coal—Murdoch's retorts—Clegg's rotary retort—Disadvantages of iron retorts—Fireclay retorts—Leakage with clay retorts—Scurfing—Early inclined retorts—Early vertical retort—Bueb's intermittent vertical retort—Dessau vertical retorts—Woodall-Duckham continuous vertical retorts—Glover-Young systems—Glover-West continuous vertical retorts—Carbonisation in bulk—Chamber carbonisation—Fully charged horizontal retorts—Glover's chamber retorts—Yield of gas from the various systems—Fuel consumption in the various systems—Advantages of the continuous vertical retort . . . . . *pp.* 64–99

CHAPTER IV

COKE OVENS AND THEIR DEVELOPMENT

The early history of coke manufacture—Meiler coke—Beehive ovens—Modern improvements—American practice—Jameson's oven—Classification of coke ovens—The Coppée oven—The Appolt oven—Simon-Carvès recovery plant oven—The Otto recovery plant oven—Difficulties of heating the chambers—Illuminating gas from recovery coke ovens in America—Results—Differences between American and Continental gas chamber processes . . . *pp.* 100–114

CHAPTER V

THE CONDITIONS EXISTING IN THE DESTRUCTIVE DISTILLATION OF COAL

Vapourisation—The effect of temperature on matter—Destructive distillation—Heat of formation—Exothermic and endothermic compounds—The work of Euchêne on the heat of formation of coal—Mahler's determinations—Researches of Constam and Kolbe on the calorific value of coals and their distillation products—Specific heat—Heat used in the distillation of coal—Economies possible—Rate of conduction of heat through walls of retort—Temperature of carbonisation—Ratio of heating surface to weight of charge—Co-efficient of conductivity of fireclay—High and low temperature carbonisation—Passage of heat in vertical retorts, chambers, and transmission of heat through ordinary charge in horizontal retorts and through fully charged horizontal retorts—The improvements obtained by using fully charged horizontal retorts—The theories of the cause of the improvement as stated by Bueb, Ste Claire Deville and others—

Temperature of charge in Dessau retort—Effect of the size of coal on the escape of the gases—Fracture of coke from horizontal retorts and coke ovens—The swelling of coal—Temperature of gas from mouthpiece of an intermittent vertical retort—Effect of pressure on the gases given on distillation—Size of coal an important factor in securing uniformity of gas—Auto-carburetting—Blass' experiments . . . . . *pp.* 115–148

CHAPTER VI

THE PRIMARY GASEOUS PRODUCTS OF THE DESTRUCTIVE DISTILLATION OF COAL, AND THE BODIES FROM WHICH IT HAS BEEN FORMED

The distillation of wood at low temperatures—Composition of the gases evolved—The gases given by wood at high temperatures—Peat—Composition of peat and its destructive distillation—Lignites and their composition—The work of Ste Claire Deville—Analysis of the coals used and the results obtained—Constam and Kolbe's experiments on coals—Reason for the differences found—Euchêne's results—Effect of oxygen in coal on the products of distillation—Composition of humus and resin bodies—Discussion on Constam and Kolbe's work—The experiments of Lewis T. Wright—Coalite—Low temperature carbonisation—The researches of Porter and Ovitz on low temperature carbonisation—The work of White, Park and Dunkerley on American coals—Messrs Burgess and Wheeler's experiments—Primary and secondary reactions . . . *pp.* 149–179

CHAPTER VII

TAR: ITS FORMATION, USE AND DECOMPOSITION

Formation of tar in the distillation of coal—Deposition of tar in the hydraulic main, condensers and scrubbers—Saturated and unsaturated hydrocarbons—The Paraffin series—Isomerism and metamerism—Naphthenes—The constituents of tar—Benzene and anilin—Naphthalene—Phenol—Creosote oil—Anthracene oil—Effect of oxygen in coal on the tar—Low temperature tar—Course of the decompositions in the distillation of coal—Comparison of tar from Dessau vertical and the horizontal retort—Lewis T. Wright's experiments on the distillation of coal—Utilisation of tar for gas-making and its limitations—Factors governing its successful use—The Dinsmore process—Tully's methane-hydrogen process—Paraffinoid tar—Benzenoid tar—Coke oven tar—Composition of tar from Simon-Carvès and Semet-Solvay ovens—Blast furnace tar—Phenoloid tar—Water gas tar . . . . . *pp.* 180–20

CHAPTER VIII

COKE

The formation of coke—Distinction between retort and oven carbonisation —Characteristics of good coking coal—Effect of oxygen on the coking properties of coal—Work of Anderson and Roberts on the coking of coal—Temperature of the formation of coke—Burgess and Wheeler's experiments on low temperature coke—Nature of the luting material in coke—Probable true cause of the binding—Effect of rate of heating on the coking of coal—Parry's researches on the gases in coke—Analysis of the ash of coals—The effect of temperature on the appearance of coke—Beehive coke—Coking in ovens—Properties of the coke yielded by various coals—Reasons for the coking of coal—Metallurgical coke—Gas Coke—The use of coke as a domestic fuel —Smoke production—The burning of coal in an ordinary grate—Special forms of grate—The distribution of heat in a domestic fire—Drawbacks to the use of coke as a domestic fuel—Low temperature coke—Coalite—Coalexld—Charco . . . . . *pp.* 208–244

CHAPTER IX

THE NITROGEN AND SULPHUR OF COAL AND THEIR RECOVERY

Utilisation of nitrogen in agriculture—Yield of ammonium sulphate from coal and shale distillation—Nitrogen in vegetation—Percentage of nitrogen in coal and peat—Nitrogen in various coals—Yield of ammonium sulphate per ton of coal—The work of Forster, Watson Smith, and M'Leod on the distribution of nitrogen in coal distillation —Beilby's estimation of the nitrogen—Nitrogen in coke—Percentage of ammonia with increase of temperature—Tervet's experiments—The work of Ramsay and Young on the yield of ammonia—Yield of ammonia per ton of coal—The liming of coal—Formation of ammonia liquor—Composition of the liquor—Coke oven and blast furnace liquors—Ammonia compounds present in the liquor—Free and fixed ammonia—The manufacture of sulphate—Theories of the formation of ammonia during distillation—The influence of dilution—Cyanogen and cyanides—Sulphur in coal—Organic sulphur compounds in coal—Disulphide of iron and its relation to spontaneous ignition . . . . . *pp.* 245–274

CHAPTER X

MODERN COAL GAS

The primary products of the decomposition of coal by heat—Secondary decompositions at low temperature—Effect of heat upon the secondary

products—Improvements in the gas obtained by new methods of carbonisation—The composition of the gas from Glover-West continuous vertical retorts—From Dessau vertical retorts—Advantages of continuous carbonisation—Composition of gas from ordinary horizontal retorts—The alteration of the standard of illuminating power—The calorific value of gases and the advantages of a calorific standard—The Settle-Padfield vertical retort—Suggestion for a continuous system of carbonisation—The autocarburetting process and its results—Its application to continuous carbonisation *pp.* 275-300

APPENDIX

Weights and measures—Measure of capacity—Useful data—Conversion factors—Table for converting degrees of the Centigrade thermometer into degrees of Fahrenheit's scale—Table of the corresponding heights of the Barometer in Millimetres and English inches—Thermal data —Weight and volume of gases—Thermal value of gaseous fuels per cubic foot and per pound—Average thermal value of fuels per pound —Liquid fuels—Gaseous fuels . . . . . *pp.* 301-311

INDEX . . . . . *pp* 313-315

LIST OF ILLUSTRATIONS

PAGE

1. DESSAU VERTICAL RETORTS 76
2. WOODALL-DUCKHAM VERTICAL RETORTS, LAUSANNE PLANT . 78
3. WOODALL-DUCKHAM RETORT, SHOWING CHARGING AND DISCHARGING ARRANGEMENTS 79
4. LONGITUDINAL SECTION OF EXTRACTOR ROLLER . . . 81
4a. CROSS SECTION OF EXTRACTOR ROLLER 81
5. EXTRACTOR DRIVER 82
6. COKE DISCHARGE 82
7. CROSS SECTION OF TOP OF RETORT 83
8. LONGITUDINAL SECTION OF TOP OF RETORT 84
9. GLOVER-YOUNG RETORT 86
10. SECTIONAL ELEVATION OF GLOVER-WEST VERTICAL RETORT HOUSE AND COAL STORE 87
11. GLOVER-WEST COKE CHAMBERS: FRONT VIEW . . . 88
12. GLOVER-WEST COKE CHAMBERS: SIDE VIEW . . . 89
13. CROSS SECTION OF THE MUNICH CARBONISING CHAMBER . 92
14. BATTERY OF FIFTEEN KOPPERS' CHAMBERS ERECTED AT THE VIENNA GASWORKS, WITH THE GAS-PURIFYING PLANT ON THE RIGHT 93
15. KLONNE'S INCLINED CHAMBER OVENS AT KONIGSBERG: CHARGING SIDE 94
15a. KLONNE'S INCLINED CHAMBER OVENS AT KONIGSBERG: DISCHARGING SIDE 95
16. CHAMBER RETORT SETTING AT NORWICH 97
17. COKE MEILER 101

PAGE

18. MODERN BEEHIVE OVEN 102

19. AMERICAN OVEN 103

20. SIMON-CARVÈS RECOVERY OVEN 107

21. OTTO RECOVERY OVEN 107

22. RISE OF TEMPERTAURE DURING CARBONISATION IN SPACE ABOVE COAL 132

22a. RISE OF TEMPERATURE DURING CARBONISATION IN CENTRE OF CHARGE 133

23. FRACTURE IN COKE IN FULLY CHARGED RETORTS . . . 141

24. FRACTURE IN COKE OVEN COKE 142

25. PHOTO-MICROGRAPHS OF COKE 242

26. SETTLE-PADFIELD VERTICAL RETORT 288

27. TOP OF SETTLE-PADFIELD RETORT 289

THE CARBONISATION OF COAL

CHAPTER I

THE FORMATION AND COMPOSITION OF COAL

Primary source of energy—The atmosphere of prehistoric days—Formation of carbon dioxide during combustion, respiration and fermentation—Decomposition of carbon dioxide by vegetation—The action of chlorophyll—Calories and British Thermal Units—Formation of vegetable deposits in the carboniferous period—Drift deposits—Action of time, temperature and pressure—Conversion of woody fibre to coal—Theories as to the nature of the change—Mineral constituents in coal—Nitrogen—Water—Cellulose and ligno-cellulose—Humic and ulmic acids—Tertiary coals, brown coals and lignites—Resin constituents—Formation of boghead cannel and shale—Theory of the constitution of coal—The binding material in coke—Weathering of coal—Spontaneous ignition—Pyrites—Ignition point of coals—Absorptive power of coals—Action of solvents on coal—Anilin and pyridine—Extraction of coal by pyridine—Water in coal—Ash of coal—Gruner's classification of coal—Microscopic character of coal.

The great generalisations which underlie all processes of change, and which we know as the conservation of energy and matter, teach us that we have not the power to create or destroy. Although we may change the form of matter to an almost endless extent, yet our powers are limited to these transmutations, and beyond this we cannot go.

The sources of energy which are at our disposal for the generation of power are gravity, muscular force and heat, and if investigation be carried further, it is found that the sun is the source of them all, and that without the sun their existence would be an impossibility. It is the energy

of the sun that causes the wonderful changes which take place during the growth of vegetation, and which over countless ages built up for us the accumulations of fuel which form our coal-fields.

In the prehistoric days, long ages before man appeared on the surface of the earth, the probabilities are that the atmosphere differed widely from that of to-day, and was far richer in carbon dioxide and more highly charged with water vapour, and that in reality it was only after countless ages of vegetable growth that an atmosphere capable of supporting the higher forms of animal life was formed.

To explain this we must consider the actions which at the present time keep the atmosphere constant, and, by creating a balance between animal and vegetable life, make both possible.

When animals or human beings breathe, the life-supporting principle of the air is exchanged for carbon dioxide, which by this process is continually being poured into the atmosphere ; and this gas is also formed during all processes of combustion, whether they be rapid, as when wood is burnt in a fire, or slow, as when vegetable matter rots away. It is also produced by processes of fermentation, and escapes in enormous quantities into the atmosphere from the earth from natural causes.

It must be remembered that during most processes which give rise to carbon dioxide, oxygen is being absorbed, and it has been computed that this takes place at the rate of over three and a half million tons per diem—a rate which would rapidly diminish the percentage of oxygen and increase that of carbon dioxide, the air being rendered unfit to support animal life.

It has, however, been shown, by the researches of Fruchot, Schultze and others, that in the open air the percentage of carbon dioxide varies but little, the average amount being four volumes in ten thousand of air—this quantity decreas-

ing during rain and increasing during frost and fog, and at night-time, but again diminishing after sunrise. It is therefore evident that there is some natural agency at work which tends to neutralise the effects of animal life and decay, and it is found that vegetable life plays an important part in this process of purification.

This regeneration is due to the rays of the sun, and the growth of vegetation is the means by which it is brought about. All the ordinary forms of plant in which the green colouring matter, known as "chlorophyll," is present owe their growth to energy derived from the sun. By its influence the chlorophyll contained in the plant cells absorbs carbon dioxide and water vapour from the atmosphere, whilst more moisture and small quantities of mineral salts are drawn in by the roots. The chlorophyll then acts on the absorbed carbon dioxide and water vapour, and a marvellous series of interactions ensues, which results in the formation of starch granules and sugars, which afterwards become practically the food of the plant, and are incorporated as the woody fibre of which the solid portion chiefly consists, the completed action being of some such nature as that expressed by the equation—

Carbon dioxide.		Water vapour.				Cellulose.		Oxygen.
$6CO_2$	+	$5H_2O$	+	Sun's energy	=	$C_6H_{10}O_5$	+	$6O_2$

It is this oxygen so liberated in the early days of the world's history which, according to some theorists, formed the atmosphere, and has since kept the oxygen present in it in a practically constant quantity.

The above equation, however, represents only the first and final stages of a series of actions and interactions, the course of which is but little understood, but the fact that the energy of the sun is necessary to bring about this change can be readily seen by the growth of vegetation when deprived

of light. Under these conditions the plant will form merely a few sickly and colourless shoots, whilst on the other hand recent experiments have shown that ordinary vegetation can be accelerated in its growth by the illumination from certain forms of artificial light during the hours of darkness.

Exhaustive researches that have been made upon plant life point to the function of the chlorophyll in the growing plant being three-fold. It is the rays in the immediate neighbourhood of the red and orange in the spectrum which are the most active in causing the assimilation of the carbon dioxide and water vapour; and the chlorophyll absorbs other rays which hinder the formation of carbohydrates, transforming rays of short wave length into those rays which most favourably affect the production of the sugars and starch, which are the food of the plant structure; and it thus also acts by the conversion of light into heat.

The usual statement that the solid matter of the plant consists of cellulose is, of course, only approximately true, as cellulose is only one of several modifications produced by the actions taking place in the growth of the plant. The chemical actions which have resulted in the formation of the cellulose have required an expenditure of energy which, in the primary decomposition of the carbon dioxide and water vapour, can be expressed in terms of the heat necessary to raise a unit weight of water one degree.

A unit weight of carbon in burning to carbon dioxide raises 8137 units of water 1° C., or 14,647 units of water 1° F. The former we speak of as "calories," and the latter as "British Thermal Units." So also a unit weight of hydrogen in burning to form water develops 34,500 calories, or 62,100 British Thermal Units (B.Th.U.), and in order to again decompose the carbon dioxide and water, so as to liberate the unit weight of carbon and of hydrogen, just the same amount of energy expressed in heat units will be absorbed. In the plant this energy has been derived from

the sun, and has been rendered partially latent in the cellulose, and when this compound is burnt as wood so as to convert the carbon and hydrogen again to carbon dioxide and water vapour, the stored energy in the form of heat is once more set free and can be utilised for heating purposes.

When the monster vegetation of the carboniferous period grew, it is evident that, although the plant forms were of a simpler structure than is found in their descendants, the actions involved in their growth were the same as those we have considered, the great difference being in the rapidity with which they grew and the size which they attained, which may be taken roughly as twenty times that of their modern types. We know the rapidity with which in tropical regions the marsh plants spring up, attain great size, and then rot down, and it was a similar action, accentuated by heat from the cooling earth below and the richness of the atmosphere in plant food, *i.e.* carbon dioxide and water vapour, that induced in the vegetation of the coal age an exuberance of growth that has never been equalled since.

The great vegetable deposits so formed rapidly accumulated, as it must be remembered that during this period decay as we now know it could not have existed—oxygen was only beginning to accumulate in the air, and the processes of slow combustion, by which nature now rids the earth of waste matter, were practically inoperative, so that nothing but what we call to-day "checked decay," *i.e.* changes at the expense of the combined oxygen in the vegetable matter, could take place, and deposits of a size that would be impossible with the atmospheric conditions now existing were easily formed.

The conversion of vegetable matter into coal gives a loss in weight of about 75 per cent., and as the specific gravity of coal will vary from about 1·1 in the lignites to 1·4 in the anthracite, the volume of coal can be only from one-ninth

to one-sixteenth the volume of the vegetable magma from which it was formed. When one considers the original depth of the vegetable deposit that gave rise to any thick coal seam—say the South Staffordshire 10-yard seam—one feels that no deposit that could form under present conditions would explain it. The Staffordshire coal would represent one-tenth to one-twelfth the volume of the original vegetation, so that the 10-yard seam represents a deposit extending over many square miles and, say, 300 feet in thickness, which, of course, even with the factor of geological time at one's disposal, would appear incredible.

An examination of the seam, however, shows it to consist of not one deposit, but twelve or thirteen ; very thin deposits, called " partings," existing in between the different parts of the seam. These partings, as the seam is traced northwards, gradually open up into wedge-shaped masses of sandstone and shale, clearly showing that the bed has been formed at the mouth of a big river, and that the various parts of the seam represent great masses of floating vegetable lumber brought down by the stream and probably deposited on the silt bank at the mouth of the river, and that as it has sunk down owing to becoming denser from partial decay, a fresh deposit has formed over it.

The vegetable deposits which the action of time, heat and pressure converted into our coal seams have many of them evidently grown *in situ*, as is shown by the underclay, which is loaded with fossil roots (stigmaria). These seams as a rule are found extending over a large area and are generally of a uniform thickness, whilst the strata in which they occur also exhibit the same uniformity.

Other coal-fields, however, evidently owe their origin to enormous masses of water-logged drift, which have been brought down by great rivers and deposited in the deeper parts of primeval seas or lakes ; seams formed in this way showing no fossil roots in the under strata, whilst the fossil

remains of marine life are frequently found in both under and over strata.

If we descend a deep mine the rise in temperature is very marked, and amounts to about 1° F. for every 65 feet we descend, and it has been estimated that at a depth of two miles the temperature would approach that of boiling water, whilst at a depth of thirty-four miles it would reach that of molten iron. We know also the changes of level that take place during earthquakes and volcanic disturbances, and the molten lava from a volcano in eruption reminds us that although the earth has been cooling down through geological ages so vast that the mind fails utterly to realise them, yet it is still only a crust of cool solid matter on which we live, and we realise faintly what the conditions must have been in the carboniferous age when the solid crust was only a small fraction of its present thickness, and contraction was taking place in every direction in the cooling earth. Changes in level and eruptive upheavings were then as frequent as they are now rare, but only a century ago an earthquake in the valley of the Mississippi lowered the level of many square miles of the country below water level, and submerged the cypress forests that were upon it, these being rapidly buried by the clay and silt washed down by the rush of water.

In the same way the monster deposits of the coal age brought by subsidences of the land below water level became covered with soil, sand and silt, and when the water drained off to some lower level vegetation again started and formed a second area of deposit, repetitions of these actions giving the various seams that we find in a coal-field. If the area on which the vegetable deposit was formed was level, the seam also would be level, but the continued contraction of the cooling earth caused a crumpling of the first formed crust, it being thrown upwards in one place and forming valleys in others, the seams being bent with the

enclosing strata, whilst when the over-bending of the crust fractured the seams and strata, the faults or breaks in the seams resulted.

It would serve no useful purpose to go more fully into the details of the geological conditions influencing the formation of the coal measures and the strata in which they are found, as this can be obtained from any standard work on geology. We can now obtain a general idea of the outline of the chemical changes taking place in the conversion of the vegetable matter into coal.

Analysis shows that the main change which the mass is undergoing whilst exposed to the action of checked decay, induced and carried on by heat and pressure through countless ages of time, consists of an elimination of carbon, hydrogen and oxygen in the form of carbon dioxide and methane.

The following table indicates the way in which the gradual elimination of the hydrogen and oxygen altered the cellulose of the growing plant to the product of our coal seams :—

THE CONVERSION OF WOODY FIBRE TO COAL.
(BUTTERFIELD.)

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash.
Cellulose . . .	44·4	6·2	49·4	...	...	...
Dry wood (average) .	48·5	6·0	43·5	0·5	...	1·5
Dry peat . . .	58·0	6·3	30·8	0·9	trace	4·0
Lignite . . .	67·0	5·1	19·5	1·1	1·0	6·3
Coal	77·0	5·0	7·0	1·5	1·5	8·0
Anthracite . . .	90·0	2·5	0·25	0·5	0·5	4·0

This action is made even more manifest by calculating the analysis so that the carbon is kept at a fixed quantity, which brings into bold relief the gradual elimination of the other constituents of the cellulose.

THE CONVERSION OF WOODY FIBRE TO COAL.
(PERCY.)

	Carbon.	Hydrogen.	Oxygen.
Wood	100	12·18	88·07
Peat	100	9·85	55·67
Lignite	100	8·37	42·42
Bituminous coal	100	6·12	21·23
Anthracite (Wales)	100	4·75	5·28
Anthracite (Pennsylvania)	100	2·84	1·74
Graphite	100	...	...

These changes in composition may also be traced in the calorific value, and show the thermal advantages gained by the elimination of the oxygen during these processes of natural distillation.

	Calories.	British Thermal Units.
Wood	4771	8,588
Peat (dry)	5600	10,080
Lignite	7000	12,600
Bituminous coal	8446	15,203
Anthracite	8677	15,618

Time alone, however, is not the only cause of the alteration in the character of the coal. Temperature and pressure play so important a part that it is unsafe to base any far-reaching ideas as to the age of a coal upon the amount of natural carbonisation which it has undergone.

So far all authorities are agreed; but the changes which take place in the conversion of the plant material into the coal, and the nature of the compounds present in the various kinds of coal, which give this body its widely diverging characteristics, still remain unsolved, in spite of the century of work which has been expended on it, and the fact that it

has been attacked from almost every point of view. Most of the theories that have been brought forward assume that the original material from which the coal has been formed is $n(C_6H_{10}O_5)$, by which empirical formula is represented the "celluloses," and in which the ratios of the atoms lend themselpes to an easy explanation of the formation of various kinds of coal by the subtraction of various proportions of the known gaseous products of checked decay taking place in the formation of peat, lignite and coal, *i.e.* methane, carbon dioxide and water.

The infiltration of water holding oxygen in solution has been held responsible for actions that have resulted in the concentration of the carbon owing to the evolution of these compounds; whilst the action has also been looked upon as one of dehydration. The conditions under which the coal has been formed, however, are so varied that both theories can find some ground for support. But all such theories assume that coal is a definite compound, and that the variations can be represented empirically by a formula. Our only knowledge of the coal plants is derived from their fossilised remains, and as the destruction in their structure has been almost complete, the evidence to be obtained is very small. But although of an entirely different, and far more simple form, the plant life of the carboniferous period from which the coal deposits have been formed must have been as divergent in character as the sphagnum of a peat bog is from the timber of a forest.

Although cellulose is the main constituent of the woody fibre of all plants, yet there are also found in it ligno-cellulose and other allied compounds, together with very varied extractive matters in the sap. Even supposing that all the plants had undergone the same treatment as regards time, temperature and pressure, it is only natural to expect that the resulting coal would show wide variations in composition; and as the conditions of formation differ more widely even

than the material dealt with, it is not to be wondered at that great variations are to be found not only in coal from separate seams in a colliery, but also between different parts of the same seam.

In addition to the difficulty caused by our ignorance of the changes that have taken place under conditions of which we know but little, and in material of the most variable composition, the coal itself behaves in such a refractory manner towards ordinary solvents and reagents, that the most we can gather about its constitution is the knowledge deduced from an ultimate analysis giving its percentage composition, or an approximate analysis showing the effect upon it of heat, in causing it to yield fixed carbon, volatile matter, moisture and ash.

The most satisfactory view to take of the composition of coal is that it is an agglomerate of the solid degradation products of vegetable decay, together with such of the original bodies as have resisted to a greater extent the actions to which the material has been subjected.

All the plants of which we have fossilised record in our coal measures consisted of sedges and reeds, tree ferns, club mosses or lycopodia, and trees akin to the pine; but in those prehistoric days the excess of carbon dioxide, warmth and moisture caused the vegetation to grow with a succulent freedom and rapidity unknown in later days, which rendered their tissues easily susceptible to decay and fermentation—actions which left only the more resistant unchanged. The work of Morris, Carruthers, Fleming and Huxley has shown us that the bituminous matter in coal is largely derived from the spores of fossil mosses akin to the lycopodia. The club mosses of to-day give in their spores the body known as lycopodium, a yellow powder of an exceedingly resinous and inflammable nature. Spores of this character from the giant growths of the carboniferous period, together with the more resinous portions of plants of the pine family,

are the substances which have best resisted the actions taking place during the ages that have elapsed in the formation of coal, and which are to be found, fossilised, but otherwise but little changed, in the coal body.

Although when considering the changes that have taken place in the formation of coal we deal only with the carbon, hydrogen and oxygen in its composition, yet coal contains other bodies, which, however, in all probability do not play any important part in the actions that lead to the change. The mineral constituents of the sap and fibre of the original vegetation may be left out of the calculation, as although the reduction of the sulphates to sulphides, and the combination of the sulphur with iron from the surrounding soil to form pyrites and organic compounds containing sulphur, and the deposition in the mass of other water-carried salts, all tend to the production of the ash of the coal, yet they affect the carbonaceous material only to a very slight extent. So also nitrogen compounds (which are found in every fuel of vegetable origin) are present in all stages of the formation from peat to coal, but their presence may be disregarded; whilst water, although probably an active factor, and also a product of some of the decompositions, cannot be taken into account in considering the actual course of the changes from analysis of the body produced. Hence, in tracing the probable course of the degradation of the vegetable matter through its various stages, it is better to ignore all such factors and deal only with the variations of the carbon, hydrogen and oxygen in the material.

In the fibre of the original plants there are found two well-defined bodies—cellulose, as represented by cotton fibre, and lignose, as represented by jute fibre. In the former the percentage of carbon is 44, in the latter 47, each giving distinctive reactions with dilute acids at 70° C., with anilin sulphate, with Schultze solution, and with mixtures of sulphuric and nitric acids. Starch is present in the cellular

tissue, and there are also present the extractive and mineral matters of the sap.

Amongst the extractive matters are gums—such as those exuding from the acacia and cherry, but also present in the juice of many plants—mucilage, vegetable jelly—the gelatinising agent of many juices—resins, essential oils and other well-defined bodies. Some of the essential oils absorb oxygen and form resins, which, being more resistant to change, accumulate in masses of decaying vegetable matter, and large quantities of them are found in the lignite beds in a fossilised state.

During the changes brought about by decay the carbohydrates and extractive matters, in the presence of moisture and air, become converted into carbon dioxide and water, but if the free access of air is checked, the action is slowed down and carbon dioxide and methane are evolved.

In a mass of rotting vegetation undergoing checked decay fermentation plays an important part, and Renault, in his researches upon peat, found that fungi and bacterial ferments were the most important factors in the conversion of vegetable fibre into peat, the resulting ulmic compounds having the composition—

Carbon	65·31
Hydrogen	3·85
Oxygen	30·84

Mulder also, at an earlier period, found that certain bodies could be extracted from peat, to which he gave the name of ulmic and humic acids; and Einof, Proust and Braconnot found that such bodies formed the chief portion of peat :—

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.
Humic acid .	60·13	4·74	31·52	3·61
Ulmic acid. .	62·03	4·65	33·33	..

Herz found bodies of the same character in lignites, which he called carbo-humic and carbo-ulmic acids, having the composition—

	Carbon.	Hydrogen.	Oxygen.
Carbo-humic acid . .	64·59	5·15	30·26
Carbo-ulmic acid . .	62·36	4·77	32·87

Fremy found that a mixture of mono-hydrated sulphuric acid and nitric acid was capable of dissolving not only lignite but bituminous coals, giving a dark brown solution, from which an ulmic compound is entirely precipitated by water ; and Anderson has shown that with similar treatment compounds of the same character can be obtained from both caking and non-caking coals.

The bodies obtained in this way are probably not definite compounds, and resemble the residues left by the action of dilute acids on sugar and starch. There seems to be no doubt, however, that in all bituminous coals there are present degradation products of a humus or ulmic nature, and these are probably the portion containing the nitrogen. The composition of such a body will approximate to—

Carbon . . .	63 per cent.
Hydrogen . . .	5 ,,
Oxygen . . .	32 ,,

The tertiary coals, like the brown coal and lignite deposits, are rich in fossil gums and resins, and a number of these have been isolated and analysed. In Friesland peat, Mulder has found resinous bodies of a similar character—

	Source.	Observer.	Analysis.			Name.
			Carbon.	Hydrogen.	Oxygen.	
Peat (dark) .	Friesland . .	Mulder . .	76·31	10·98	12·71	Beta-resin.
,, .	,, . .	,, . .	78·05	11·94	10·01	Gamma-resin.
,, .	,, . .	,, . .	79·70	12·15	8·15	Delta-resin.
Peat (light) .	,, . .	,, . .	75·12	10·21	14·67	Alpha-resin.
,, .	,, . .	,, . .	79·43	12·54	8·03	Gamma-resin.
Lignite . .	Saxony . .	Wackenroder .	78·20	12·30	9·50	Cerinin.
,, . .	,, . .	,, .	81·97	11·47	6·56	Leucopetrin.
,, . .	,, . .	Bruckner . .	77·35	10·20	12·45	Georetic acid.
,, . .	,, . .	,, . .	80·27	13·37	6·36	Geomyricin.
,, . .	,, . .	,, . .	78·64	12·70	8·66	Geoceric acid.
,, .	New Zealand .	Hauer . .	76·53	10·48	12·80	Ambrite.
,, .	Bohemia . .	Laurentz . .	81·47	8·71	9·82	Anthracoxene.
,, . .	Moravia . .	Schrotter . .	80·40	10·68	8·74	Retinite.
	Mean . . .		78·65	11·36	9·88	

From these figures it will be seen that there is but little difference between the products from the lignite and Mulder's peat resins; whilst it is interesting to note that in the lignite beds of Saxony layers of opaque, yellowish-brown matter are found (the pyropissite of Kenngott) which yield up to 62 per cent. of paraffin on distillation, and is the body from which Wackenroder and Bruckner extracted their resins, and bodies of the same character have been repeatedly extracted from coal. It is evident, therefore, that in coal there are resin bodies approximating to the general composition :—

Carbon . . .	75 per cent.
Hydrogen . . .	11 ,,
Oxygen . . .	10 ,,

The amount of resin constituents in the original vegetation, and which concentrates itself in the coal, must play an important part in the chemical changes taking place during the formation and ultimate composition of the coal; and although the plants that flourished in the coal age were of a very different character to those of later periods, yet in all probability the variations in their extractive matters differed to much the same extent as in the flora of to-day. Thus, some deposits would be formed from vegetation containing but little of the resin-forming constituents, whilst others would be rich in them. This difference makes itself evident in the physical characteristics of the lignites, which are sometimes more like wood than coal, whilst at others they are black and shining, and with a conchoidal fracture; these variations in appearance being due to the conditions under which they have been formed and to the amount of resin-forming constituents present.

The resin constituents as they exist in the peat deposits of to-day are present only to the extent of 5 to 10 per cent., but in the decaying vegetation of the carboniferous period

the percentage was probably much higher. The humus, unprotected by it, rapidly undergoes decomposition, with concentration of carbon and evolution of methane, carbon dioxide and water. With increase in the thickness of deposit the temperature probably rises, and the ratio of resin constituents advancing in proportion to the concentration, binds together the mass, and forms a protection to the remaining humus, with the result that after the lapse of centuries lignite is formed. If the amount of resin constituents has been small or has been distributed unevenly throughout the mass, the lignite is loose in structure, and during the ensuing ages continues decomposing until, if the pressure has been great and the temperature high, nothing but the residual basis of carbon and trace of resin constituent are left, in the form of steam coal or anthracite. Under other conditions they may remain mixed with the bituminous coal in a seam, and form the " mother of coal."

With a high proportion of resin bodies on the other hand—as in the case of a drifted deposit of spores from lycopodia—and with a high temperature, the resins may become semi-liquid, and, mingling with the surrounding earthy deposits, will give such compounds as boghead cannel, the organic matter of which has the same composition as resin, whilst the ash amounts to 33 per cent. Some of the so-called cannels, however, are simply very rich bituminous coals. When the temperature has been high enough, some of the resin constituents practically distil into the underlying clay, yielding some forms of shale.

Isomeric and other changes in the resin bodies may be brought about by heat, whereby their behaviour to solvents is altered. When the heat is accompanied by pressure, the resins are in some cases decomposed, forming various hydrocarbons, a long series of which were isolated by Renard. Hydrocarbons like retene ($C_{18}H_{18}$) have frequently been isolated, and this body is found in many lignites. Within

the last few months Pictet and Ramseyer have isolated hexahydrofluorene ($C_{13}H_{16}$) and others of the hydro-aromatic hydrocarbons from coal—bodies which are resolved into aromatic hydrocarbons and hydrogen on destructive distillation. Renard long ago isolated not only saturated hydrocarbons like pentane and hexane, but also hexahydrides or naphthenes isomeric with the ethylene series, from the resin oil obtained by distilling wood resin at a low temperature (350° C.—632° F.); among these hexahydrides being C_7H_{14}, C_9H_{18}, and $C_{10}H_{20}$. The presence of bodies of this character in low temperature coal tar is a further proof of the presence of the resin bodies in coal, whilst one knows the amount of higher paraffins that are present in peat.

All these degradation products of the original vegetation are to be found in the bituminous coals, the residual body and humus forming the basis, which is luted together by the hydrocarbons and resins; and the characteristics of the various kinds of coal owe their variations to the proportions in which the four groups of the conglomerate are present. Each of these constituents of the coal has its own characteristic products of decomposition when the coal is carbonised; the humus bodies yield a large proportion of the gaseous products, and show no sign of melting, but begin to break up at about 300° C. (572° F.). With increase in temperature the decomposition becomes more rapid; water distils over in the early stages, the tar is thin and poor in quantity, and the gases up to 600° C. (1112° F.) consist of hydrogen, methane and carbon dioxide, with smaller quantities of carbon monoxide and traces of other saturated hydrocarbons. The decomposition can be completed below 800° C. (1472° F.), but if the temperature be run up to 1000° C. (1832° F.), the amount of carbon monoxide increases owing to the reduction of some of the carbon dioxide by the red-hot carbon, whilst hydrogen and methane are still evolved.

If the humus be slowly heated, a large proportion of the

oxygen is given off in combination with hydrogen as water vapour, but if the temperature be raised quickly a larger proportion combines with carbon to form carbon monoxide and dioxide. The residue shows no sign of caking, whilst it requires a large proportion of cementing material to make the particles cohere. The resin bodies and hydrocarbons which form the cementing portion in the coal melt between 300° and 320° C. (577° and 606° F.), and if a coarsely powdered sample of the coal becomes pasty or semi-fluid at this temperature, it is a strong indication that the coal will coke on carbonisation—a fact noted by Anderson, and which has proved very useful, in practice, as a rough test. About these temperatures also the resin bodies and hydrocarbons begin to decompose.

At low temperatures the resin bodies yield saturated hydrocarbons, unsaturated, chiefly hexahydrides or naphthenes, together with some oxygenated compounds. The hydrocarbons yield paraffins and liquid products, and all these primary constituents undergo further decompositions at slightly higher temperatures. The liquids so produced distil out as tar vapours and hydrocarbon gases, and leave behind the residuum pitch, which at 500° C. (932° F.) forms a mass already well caked together if the residuum from the humus is not too large in quantity. The coke formed at this temperature is soft, but if it be now heated to 1000° C. (1800° F.) the pitch residue is decomposed still further, yielding gas and leaving carbon, which binds the mass into a hard coke.

Muck, and other observers have shown that it is not always the coal which is richest in volatile matter that evolves gas most rapidly or yields the most hydrocarbons. This naturally follows from the fact that the coals which have the highest oxygen content are mostly those giving high volatile matter. As these are rich in humus bodies which yield most of the diluting gas, and but little tar or rich

hydrocarbon gases, they cannot give the high result of a coal in which the oxygen content is about 10 per cent. or rather lower, and which contains a large percentage of resin bodies.

Many theories have been put forward as to the nature of the binding material in coke. Some declare that it is the residuum of the semi-fused constituents of coal, whilst Wedding and others consider that it is carbon deposited by the decomposition of heavy hydrocarbon vapours, which is undoubtedly the cause of the carbon hairs found in coking. It seems most probable, however, that the cementing material is due to liquid products, the most volatile of which are driven off as vapours, leaving pitch, which carbonises and binds the mass into coke.

The binding material must be formed below 450° C. (842° F.), as if a good coking coal be carbonised at 450° C., a coke is obtained which, although not strong, is perfectly luted together. If this low temperature coke be powdered and again carbonised, a large yield of poor gas is evolved, but no coking takes place. There can be no doubt that the coking is due to the tar derived from the resins and hydrocarbons in the coal, which on heating leaves the pitch by which the coke is luted together.

These resin bodies also play a very important, if not the chief, part in the weathering of coal. The weathering of coal is a phenomenon which depends upon the absorption of oxygen from the air. This weathering is fatal to the coking of some kinds of coal, the slacks of which are so susceptible to oxidation that a few days' or weeks' exposure destroys their coking power. Some vegetable resins, such as copal, are well known to have the power of absorbing oxygen with great rapidity, and common resin itself has been formed by the oxidation of turpentine. These bodies then are the compounds in the coal most likely to possess this property of absorbing oxygen, and it is the chemical

action so caused which leads to slow combustion, and when accelerated by any rise in the surrounding temperature is capable of causing the spontaneous ignition of masses of coal.

The spontaneous ignition of coal has been the cause of an enormous number of serious accidents. The earliest theory as to its cause was that it was due to the heat given out during the oxidation of the pyrites or "coal brasses," which are compounds of sulphur and iron, and are present in varying quantities in nearly all coal. This idea has to a certain extent held its ground up to the present time, in spite of the researches of Dr Richters, who nearly twenty-five years ago showed that the explanation was an erroneous one. Even earlier, in 1864, Dr Percy pointed out that the cause of spontaneous ignition was probably the oxidation of the coal, and that the pyrites had but little to do with it.

Pyrites is found in coal in several different forms, sometimes as a dark powder closely resembling coal itself, and, in larger quantities, in thin golden-looking layers in the cleavage of the coal, whilst sometimes it is found in masses and veins of considerable size. These masses, however, are very heavy, and are carefully picked out from the coal and utilised in various manufactures. The yellow pyrites and even the dark varieties, when in the crystalline form, remain practically unaltered even after long exposure to air and moisture, but the amorphous and finely divided portions will oxidise and effloresce with great rapidity. It is during this oxidation that the heat is supposed to be generated.

Some coals that are liable to spontaneous ignition contain only 0·8 per cent. of pyrites. If we imagine this to be concentrated in one spot instead of being spread over the whole mass, and to be oxidised in a few hours, the temperature would rise only a few degrees, and under ordinary circumstances this rise in temperature would be practically inappreciable.

The oxidation of masses of pyrites under certain conditions gives rise to the formation of ferrous sulphate and sulphur dioxide, with liberation of sulphur, and one might easily imagine that this free sulphur, which has an ignition point of 250° C. (482° F.), would play an important part in the action by lowering the point of ignition. This, however, could happen only with larger masses of pyrites undergoing oxidation. With the small amount of pyrites present in coal, supposing air were present in sufficient quantity to oxidise it, the sulphur formed would be converted into sulphur dioxide at temperatures as low as 60° C. (140° F.). This oxidation of sulphur at low temperatures is an action not generally known, but it takes place with considerable rapidity. The only way in which pyrites can assist the spontaneous ignition of coal is that when it oxidises it helps the general rise of temperature, and by swelling splits up the coal, thus exposing fresh surfaces to the action of the atmospheric oxygen.

The igniting points of different kinds of coal vary considerably—

Cannel coal .	ignites at	668° F.=370° C.
Hartlepool coal	,,	766° F.=408° C.
Lignite coal .	,,	842° F.=450° C.
Welsh steam coal	,,	870° F.=477° C.

So that it is impossible for the small trace of pyrites scattered through a large mass of coal and slowly undergoing oxidation to raise the temperature to the necessary degree.

When coal is heating a distinctive and penetrating odour is evolved, which is the same as that noticed when wood is scorched. The gases produced consist of nitrogen, water vapour, carbon dioxide, carbon monoxide, hydrocarbons of the paraffin series, and sulphuretted hydrogen, the presence of the latter gas showing beyond doubt that oxidation of the sulphur has little or nothing to do with the action.

Ever since coal has been generally adopted as a fuel it has been recognised that great care was necessary in the storing and shipment of masses exceeding 1000 tons. If the coal has been stored wet or in a broken state, firing or heating of the mass has frequently taken place. Much inconvenience and loss has been caused by this on shore, but the real danger has occurred during shipment; and owing to this many a vessel has been lost with all hands, without any record of the calamity reaching shore.

Owing to the greater facility for treating coal when it becomes heated on shore in coal stores and gasworks, absolute ignition takes place only rarely, and it is from evidence obtained in the case of coal cargoes that we learn most as to the causes which lead to it.

Certain kinds of coal exhibit the same power of absorbing gases which charcoal has, although to a less degree. The absorptive power of new coal, due to this surface attraction, varies, but the least absorbent will take up one and a quarter times its own volume of oxygen, whilst some coals absorb more than three times their volume of the gas, which gives rise to an increase in temperature from compression, and tends to accelerate the action which is going on, but is rarely sufficient to bring about spontaneous ignition. As only about one-third the amount of oxygen is absorbed by coal that is taken up by charcoal, the action is much slower, and tends to prevent the temperature reaching the high ignition point of the coal.

When coal absorbs oxygen the compressed gas becomes chemically very active, and soon commences to combine with the carbon and hydrogen of the resinous portions, converting them into carbon dioxide and water vapour. As the temperature rises so this chemical activity increases, so that the heat generated by the absorption of the oxygen causes the oxygen to enter rapidly into chemical combination. This kind of chemical combination—oxidation—is

always accompanied by heat, and this further rise of temperature helps the rapidity of oxidation, so that the temperature rises steadily. When this takes place in a large mass of coal, which, from physical causes, is an admirable non-conductor, it will often cause such heating of the mass that, if sufficient air can pass into the heap in order to continue the action, the igniting point of the coal will be reached.

It has been suggested that very bituminous coals, such as cannel and shale, are liable to spontaneous ignition from the fact that heavy oils would exude from them on a rise of temperature, and that these by oxidising might produce rapid heating. Experiment, however, shows that this is not the case, and that the heavy mineral oils have a decided effect in retarding heating.

We can now trace the actions which culminate in ignition. As soon as the coal is brought to bank, absorption of oxygen commences, but, except under rare conditions, the coal does not heat to any great extent, as the exposed surface is comparatively small, and the size of the masses allows of the air having free access to all parts, so keeping down the temperature. After the coal has been screened and the large pieces of pyrites picked out, it is put in trucks. Here it begins to get broken up, owing to the many joltings and shuntings, and so offers a larger surface to the action of the air. When it has arrived at the ship it is further broken up by being shot down the tips or shoots. More harm is done at this than at any other period, for the coal is broken by reason of the distance it has to fall, and, as it has to bear the impact of every succeeding load falling upon it, it rapidly becomes slack, so that under the hatchway of the ship there is a dense mass of small coal. This soon rises in temperature by reason of the large surface exposed to the air, and the consequent absorption of oxygen. This sets up chemical combination between the oxygen absorbed by the coal and the hydrocarbons, and in some cases culminates in combustion.

It is found that the mass of coal exercises a most important action in the liability to spontaneous combustion. Although with cargoes of 500 tons of coal cases of spontaneous combustion amount to only about a quarter of a per cent., when the bulk is increased to 2000 tons the amount rises to 9 per cent. This is due to the fact that the larger the cargo the more non-conducting material will there be to keep in the heat, and also to the fact that the breaking up of the coal and the exposing of fresh surfaces will, of course, increase with increase in mass. It is also found that coal cargoes sent to European ports rarely undergo spontaneous combustion, whilst the number of cases rises to a startling extent in shipments made to Asia, Africa and America. This result is due partly to the length of time the cargo is in the vessel, the absorption and oxidation being a comparatively slow process, but the main cause is the increase of heat in the tropics, which causes the action to become more rapid. If statistics had been taken, most of the ships would have been found to have developed active combustion somewhere about the neighbourhood of the Cape, the action fostered in the tropics having raised the temperature to the igniting point by that time.

Moisture has a most remarkable effect upon the spontaneous ignition of coal. The absorption of oxygen is at first retarded by external wetting, but after a time the presence of moisture accelerates the action of the absorbed oxygen upon the coal, and so causes a serious increase of heat. The researches of Cowper, Baker, Dixon and others have of late years so fully shown the important part which moisture plays in actions of this kind, that it is now recognised as a most important factor.

In order to prevent the spontaneous ignition of large masses of coal, it is manifest that every precaution should be taken during loading or storing to prevent crushing of the coal. On no account must a large accumulation of small

coal be allowed. Where possible the depth of coal in the store should not exceed 6 to 8 feet, and under no conditions must steam pipes or flues be allowed so near the mass of coal as to give rise to any increase of temperature.

Professor Threlfall has advocated the wetting of coal cargoes as a preventative for spontaneous ignition. If 15 per cent. or over of water were added to the cargo it would probably prove efficacious, but the increase in weight, or rather the reduction in the amount of coal the ship could carry, would prove a serious drawback, whilst the addition of a smaller quantity of water or only partial treatment of the cargo would be an active danger.

Boudouard has shown that humus bodies are produced when coal is weathered, and the coking power is thereby lessened or destroyed. In seven samples of various coals the humus constituents were increased by the oxidation, which seems to show that the action of the absorbed oxygen is to attack the resin compounds. An excellent example of this fact showed itself during the great coal strike of 1912, when the gas companies had to clear out all their old stores of coal, when it was found that in nearly every case it had lost all its coking properties.

As we know that carbon dioxide and moisture form the chief products of the earlier stages of the heating of masses of coal, it seems probable that the result is a conversion of resinic into humus bodies with evolution of these gases. It is this change that leads to the serious deterioration in the gas and tar made from coal which has been too long in store ; whilst the fact that a cannel coal like boghead or a shale does not weather to the same extent is due partly to its dense structure, and also, in the same way, is an indication that the resin bodies of which it is chiefly composed are of a different type—a fact borne out by their resistance to certain coal solvents which freely attack the ordinary resin matter.

The lines of research intended to throw light upon the composition of coal have been either to distil the coal at various temperatures and to draw inferences from the products as to the nature of the original substance, or to attack the coal directly by means of solvents.

The early attempts to isolate definite bodies from coal by solvents were none of them very successful. Ether alcohol, petroleum ether and benzol proved to have but little solvent action. Guignet, by the use of phenol, succeeded in extracting a small quantity of a brown amorphous body from a bituminous coal, but did not identify it. In 1894 Professor Bedson reported to the British Association the results of a long series of experiments in which, besides these solvents, he also tried acetic anhydride, glacial acetic acid, turpentine and anilin (the latter solvent proving the most successful), extracting from the coal a body of the same character as that obtained by Guignet, which, when treated with benzene and ether, yielded on evaporation bodies of a resinous nature. He also found that when finely divided coal is suspended in boiling water and permanganate of potash is added, oxidation of some constituents of the coal ensues, and a dark brown alkaline liquid is formed.

In a further report in 1896 he gave the results of acting upon coal with hydrochloric acid and potassium chlorate, and showed that chlorinated compounds are formed of the same character as those obtained by Cross and Bevan from jute fibre. Bedson made a great advance in this line of research when, in 1899, he pointed out the solvent power of pyridine bases extracted from coal tar, which dissolved 16 to 18 per cent. of a Durham coal, but had no action on anthracite.

In 1901 Baker experimented upon the action of this solvent on several coals. He found that from Durham coal (Hutton seam) 20·4 per cent. could be extracted with pyridine, and that after extraction the residue had lost the

coking properties of the original coal. This observation was confirmed by Anderson and Henderson in 1902, who tried the action of pyridine in a research upon the coals of Bengal and Japan, and also upon some Scotch coals the coking powers of which were known. They found that the extraction of a strongly coking coal by pyridine weakened the coke, whilst with inferior coking coal the property is entirely destroyed.

In 1908 Professor Bedson read a paper before the Society of Chemical Industry, in which he gave the results of experiments upon six coals obtained from the Redheugh gasworks, which seem to show that with some gas coals an amount equal to practically the whole of the volatile matter capable of being driven off by heat can be extracted by pyridine.

	Volatile matter, per cent.	Pyridine extract, per cent.	Gasworks yield, c. ft. per ton.	Candle power.
I. .	34·10	32·36	11,381	16·63
II. .	33·28	35·59	11,392	16·50
III. .	31·91	24·58	11,646	16·40
IV. .	31·70	22·81	11,108	16·00
V. .	33·65	29·97	10,913	16·39
VI. .	30·87	22·53	10,730	15·76

Now from these figures the inference is that in a coal like II everything besides the fixed carbon and ash has been dissolved—that is, the humus, resin and hydrocarbon bodies —and it would have been of the greatest interest had Professor Bedson made an analysis of the residue, or at any rate had shown that no volatile matter was left in it.

The humus bodies in coal are by far the most resistant portion of the volatile matter to the solvent action of the pyridine, and are practically insoluble. But there are undoubtedly some forms of resin constituents in coal which are

nearly insoluble. Bedson found that the volatile matter in cannel coal varied very much in its solubility, whilst the hydrocarbons in shale were insoluble. Yet the destructive distillation of these bodies showed them to be very rich in resin constituents or derivations. It appears probable that in a feebly coking coal the coking property is due almost entirely to the soluble form of resin constituent, and can therefore be entirely removed by extraction with pyridine, whilst on the other hand, in strongly coking coals the property is due partly to soluble resin bodies, but to an even greater extent to other hydrocarbons of resinic origin which resist the solvent action of the pyridine, so that the coking property is weakened but not entirely destroyed by extraction.

A similar conclusion was arrived at by Anderson and Roberts in 1898 from an entirely different point of view. Dr Percy, more than fifty years ago, pointed out the fatal effect of weathering upon certain coals and slacks, and showed that if a fairly good coking coal was kept at a temperature of 300° C. (572° F.) for a few hours, and was afterwards heated to redness, it did not swell and coke. Anderson and Roberts, in trying this with various Scotch coals, found that, although it was true for a coal of medium coking power, a really strongly coking coal had the power only weakened. They found also that the same phenomenon could be brought about by treating the two coals with sodium hydrate. The conclusion is that, although resinous bodies which can be saponified or oxidised contribute largely to the coking, yet there are also present non-saponifiable bodies which, in breaking up under the influence of heat, yield enough luting to form coke. The action of pyridine seems to point to this non-saponifiable body or bodies as consisting of substances very probably akin to those found in shale and some cannels.

Burgess and Wheeler, in a paper read before the Chemical Society in 1911, took a Silkstone coal containing 33·4 per

cent. of volatile matter, and succeeded in extracting 30 per cent. by means of pyridine, leaving a coke-like residue, which on distillation at 900° C. (1632° F.) yielded hydrogen and oxides of carbon, whilst the extract on destructive distillation yielded a mixture of the paraffin hydrocarbons and hydrogen. At first sight this looks as if pyridine was a solvent which could be used to separate the humus and resin constituents. Messrs Burgess and Wheeler, however, are careful to point out that "they hesitate to identify absolutely the paraffin-yielding constituents of coal with that portion extracted by pyridine."

They are wise in being cautious, as there are several anomalies to be cleared up. Several times it has been found that after extraction the residue contains as much, and sometimes more, volatile matter than the original coal, in spite of repeated washings with acid, drying in vacuo, and other forms of treatment intended to eliminate all the pyridine. The composition of the extract also shows anomalous results. After the most careful measures have been taken to free it from pyridine, it will sometimes contain more nitrogen than did the original coal.

So far, the two most successful coal solvents have been anilin and pyridine, both of them alkaline organic bases, and as we have seen that the effect of extraction by pyridine has been the same upon the coking power of the coal as treatment with sodium hydrate, which saponifies the resin constituents, it seems highly probable that the pyridine forms a compound with the resin constituents or some portion of them. This compound is soluble in excess of pyridine, and if this is so, it should be traceable by the presence of nitrogen in the extract.

In an experiment made by Baker, coal from the Hutton seam was treated with pyridine. The residue and extract having been carefully freed from pyridine, they were analysed, with the following results :—

20·4 PER CENT. EXTRACTED.

	Original Coal.	Residue.	Extract.
Carbon . . .	80·82	82·06	79·37
Hydrogen . .	4·66	4·85	5·79
Oxygen . . .	10·81	9·65	10·73
Nitrogen . . .	1·84	1·78	2·66
Sulphur . . .	1·84	1·23	1·40

He queries the nitrogen in the extract, evidently thinking it a mistake.

Anderson also analysed a Bannockburn main coal, and the matter extracted from it by pyridine—

12·6 PER CENT. EXTRACTED.

	Original Coal.	Extract.
Carbon . . .	86·70	83·39
Hydrogen . . .	5·38	6·05
Oxygen . . .	5·94	7·30
Nitrogen . . .	1·98	2·86

In each case there was a large increase in the nitrogen. Baker's analysis of the residue shows that it did not come from the coal. The probabilities are that the extract is a feeble compound of the resin body and pyridine. In the case of the Hutton coal the coking power was destroyed by extraction, and in the case of the Bannockburn coal weakened. The extracts when distilled gave very large volumes of rich gas and left a strong but intumescent coke. The residues after extraction show a still more remarkable anomaly. As it is manifestly the resin constituent which has been extracted, one would expect that on determining the volatile matter in the residue it would be found to be as much lower as the amount extracted, but it proves to

be nearly as high as, and in many cases higher than, in the original coal.

Anderson and Henderson in their examination of coals by pyridine give the loss of weight of the residues from the extraction on heating, which are here contrasted with the original volatile matter in the coal—

Volatile.	I.	II.	III.	IV.	V.
In original coal . . .	31·98	39·89	46·59	27·4	36·78
In residue	39·26	44·14	49·14	29·6	43·02
Per cent. extracted . .	10·8	7·0	21·7	12·8	14·5

This increase in the amount of volatile matter present in coal can mean only that the pyridine has attached itself to some constituent in the coal to form a compound insoluble in excess of pyridine; but the only analysis published with the percentage of nitrogen determined (Baker) shows no sign of this, as the nitrogen is a little lower than in the original coal. The volatile matter in the residue, however, is not given.

In an experiment upon a Durham coal (Londonderry), made in my laboratory, the following results were obtained. The coal lost 18 per cent. of its weight to the pyridine :—

	Original, ash and moisture free.	Residue from pyridine.	Pyridine extract, 18 per cent.
Carbon . .	82·87	79·15	81·04
Hydrogen . .	5·57	4·71	7·18
Oxygen . .	8·72	14·00	7·98 [1]
Nitrogen . .	1·68	2·14	3·80
Sulphur . .	1·16	not deter.	not deter.
Fixed carbon .	63·00	64·46	,,
Volatile . .	37·00	35·54	,,

[1] Oxygen *plus* sulphur.

In this determination the increase in nitrogen over the amount present in the original coal in both residue and extract points to the presence of compounds of pyridine in both ; whilst the increase in hydrogen in the extract, taken in conjunction with the decrease of hydrogen in the residue, points to its having been a resin body that was dissolved.

These considerations seem to make it clear that the resin constituents condition the coking of coal during destructive distillation, and that they are of at least two kinds—the one easily oxidisable, soluble in pyridine, and saponifiable by alkalies, and which on weathering is oxidised into a humus body with evolution of water and carbon dioxide, and is responsible for the heating of coal ; the other class non-oxidisable, not saponified by alkalies, and forming with pyridine a compound insoluble in excess of the solvent. This class may be the compounds from decomposed resins, as the residue in which they are present yields rich liquid hydrocarbons as tar and pitch, but no gas.

My own opinion is that, although pyridine is a better solvent for coal than any other of which we know, it will never prove more than a useful first step in the separation and identification of the complex mixtures present in the coal. Even then pyridine has an awkward knack of attaching itself to other molecules, which make it difficult to get rid of without using such drastic methods as are quite likely to alter the nature of the bodies dissolved in it. Several observers are at work upon the problem, and it is to be hoped that satisfactory results will soon throw light upon this complicated subject.

Coal always contains a certain proportion of water, which appears to be partly mechanically held and partly in some form of combination. In this it resembles wood, which, after long air-drying, still retains an average of 20 per cent. of moisture, which, if got rid of at an elevated temperature, is reabsorbed from the air. The mechanically held portion

is generally known as "pit-water," and represents ordinary wetting, which can be got rid of by air-drying; but the so-called "hygroscopic water" is driven out only by drying at 105° C. (221° F.). As this heating for some hours causes oxidation of the resin bodies, it also tends to destroy the coking properties of the sample—a result which has led some observers to conclude that hygroscopic water is essential to coking, which is manifestly incorrect, as the tertiary coals, which contain the largest quantity of hygroscopic moisture, will not coke, owing to the proportion of humus derivatives being largely in excess of the resin bodies.

The ash of coal represents mineral constituents present in the sap of the original plant or derived from the surrounding strata during the formation of the coal; whilst nitrogen, from the proteid bodies in the vegetation, is always present to the extent of 1 to 2 per cent., and is probably mostly borne by the humus bodies in the coal, which also are the most likely to be the carriers of the organic sulphur present. The bulk of the sulphur, however, is in the form of pyrites produced by sulphides from the reduction of mineral sulphates reacting upon iron salts infiltrating in solution into the coal measures.

Many classifications of coal have been suggested and will be discussed fully in the next chapter. Some of these are based on their chemical, some on their physical, and others on their coking properties. Of the latter, the most generally adopted is that suggested by Gruner, in which he tabulates bituminous coals into five classes. Although Schondorff, Muck and others have shown that it is not applicable to all kinds of coal, this criticism also applies to all the classifications that have been proposed.

This arrangement shows not only the coking properties, but also the changes in composition which the coal undergoes, the concentration of carbon, and reduction in highly oxidised bodies. In the first class are the dry coals, yielding

		Carbon.	Hydrogen.	Oxygen.
1. Dry coal . .	Long flame and non-coking	75–80	4·3–5·5	13·0–18·5
2. Fat gas coal .	Coke porous and brittle	80–85	5·0–5·8	10·0–13·2
3. Semi-fat or furnace coal	Good coke, but porous	84–89	5·0–5·5	5·5–10·0
4. Coking coal .	Best coke	89–91	4·5–5·5	4·5–5·5
5. Lean coals and Anthracite	Non-coking	90–93	3·0–4·3	3·0–4·5

large volumes of gas and liquid products on distillation. These—as might be expected—most resemble the lignites, and share with them the property of non-coking or binding together of the residue on carbonisation. This is due to the fact that the humus bodies are still present in much larger quantities than the resinic compounds and hydrocarbons; and as on distillation they leave no binding material in the residue, the resinic bodies cannot supply enough to give more than a friable mass.

In the second class of coals altered conditions of temperature, pressure and time have led to further decompositions of the humus bodies; and the resinic constituents and hydrocarbons having increased in ratio by concentration, a point is reached at which coking takes place, although not of a really satisfactory character.

In the third class the action has continued with further concentration of the resin bodies, hydrocarbons and residuum, with the result that the former bodies are so increased in comparison to the humus and residuum that a good coke results, although it is rather too porous and bulky.

In the fourth class the proportion of resin and hydrocarbon bodies has reached the right ratio as compared with the humus and residuum, and the best coking coal is obtained. Bituminous coals of the kind classified by Gruner may therefore be looked upon as an agglomerate of humus and the

degradation products of these bodies down to carbon, luted and protected by resin bodies and their derivatives ; steam coal and anthracite as the degradation products of humus which has nearly completed its decomposition owing to the small quantity of resin bodies in the original vegetation ; cannel coal as consisting mainly of resin bodies, which, having been in a semi-fluid condition, have mingled with the surrounding earthy matter, so occasioning the high ash found in many kinds.

In this theory as to the composition of coal, it must be distinctly understood that by the terms " humus " or " resin bodies " any one definite compound is not implied, but merely bodies of this character—the humus bodies all containing a percentage of hydrogen from 5 per cent. downwards, whilst the resin bodies all contain above 5 per cent. of hydrogen. If it is once admitted that coal is a conglomerate of the kind indicated, it explains all those obscure points which no other theory touches—such as why with two coals of almost identical composition and of high oxygen content, one should be a coking and the other a non-coking coal, the reason being that in the one the high oxygen content is due to humus bodies, which will not coke, owing to the low pitch-forming nature of the hydrocarbons, whilst with the other the oxygen is due to resin bodies, which are essential to good coking.

In 1898 Anderson and Roberts made a long research upon the chemical properties of Scotch coals, and came to the conclusion that a considerable part of the organic matter in coal consists of a complex compound comparatively rich in nitrogen and also containing sulphur, and that there is also present resinous material, whilst the remaining constituents are composed of degradation products of the original carbohydrates of the coal plants—a theory which in its essentials agrees very well with the author's views on the subject.

In 1911 Burgess and Wheeler published the results of a

series of experiments upon the distillation of coals at various temperatures, which led them to conclude that coal contains two types of compounds of different degrees of ease of decomposition. The more unstable decomposes below 750° C. (1382° F.), and yields on distillation the paraffin hydrocarbons and no hydrogen: the other decomposes only at or above 750° C. and yields hydrogen only, or possibly hydrogen and oxides of carbon. The latter they suppose to be a degradation product of cellulose; the former to be derived from the resins and gums from the coal plants. The authors consider that the difference between one coal and another is determined by the proportion in which these two types exist in the coal.

In Mills and Rowan's "Treatise on Fuel," which forms the first volume of Groves and Thorp's "Chemical Technology," page 37, will be found the following remarks with regard to the microscopical character of coal.

"A transparent microscopic section of coal is seen to be composed of three very obviously distinct materials, differing in appearance and properties. These materials are—

1. An opaque black substance.
2. A yellow or reddish substance.
3. An earthy matter sometimes more or less coloured.

"The relative proportions in which these substances are associated evidently influence the various products derived from them. This is very obvious when the microscopic appearance is contrasted with the chemical constitution, and more especially with the gaseous and liquid products of their distillation, and which would appear to be peculiarly dependent upon the yellow or reddish coloured substances.

"The black substance corresponds microscopically in appearance, and in reaction, with carbon as it is known to exist in the granular or amorphous state in various mineral substances in nature. It is insoluble in sulphuric

and hydrochloric acids, and in dilute nitric acid, in caustic ammonia and potash, and chlorine is without any action on the colour.

"The third body named, the earthy matter, is more or less soluble in water, to which it sometimes communicates a colour, and consists chiefly of the substance known as umber.

"The nature of the second substance is not so easily ascertained. Its colour varies from a light yellow to a bright red or amber-coloured resinous-looking matter. It is volatilised by heat and insoluble in oil of tar, naphtha, hydrochloric acid, and nitric acid. When free bitumen is present it colours the naphtha.

"It may be generally stated that the black matter forms the chief and almost exclusive constituent of household and anthracite coals, whilst the yellow matter, on the contrary, enters most abundantly into the structure of gas coal. It is also worthy of observation that the external blackness of the coal is no criterion of the presence or absence of the yellow matter, as shown by the investigation of the nature and properties of the Pelton, Nova Scotia, Boghead, Wigan, and similar gas coals."

It is clear that (putting detail on one side until our knowledge has been broadened by experience) the answer to the question as to what is the composition of coal—whether it be derived from a consideration of the actions taking place during its formation and of the substances from which it was derived, or is obtained from analytical data, as was done by Anderson and Roberts, or from the products of distillation, as has been done by Burgess and Wheeler—must be that coal is a conglomerate of humus and its degradation products with the resinic bodies and their derivatives.

CHAPTER II

THE CLASSIFICATION AND DISTRIBUTION OF COAL

Bituminous coal—Brown coals and lignites—Classification of coals by chemical composition—Proposed classifications of Fleck, Hilt and Parr—Gruner—Seyler's tabulation—Diagrammatic representation of the formation of coal—Ratio of the constituents of coal—Composition of peat and lignites—Calorific value of coal and coal constituents—Practical application to theory—Calorific value of humus—Work of Brame and Cowan and Constam and Kolbe on the calorific value of coals—The English coal-fields and their characteristics—Coal: Total quantity and production—Percentage of coal utilised for various purposes—Possible economies in coal consumption.

Coals are classified, according to the geological age of their formation, as carboniferous or tertiary.

The carboniferous coals consist of the true coals, which range from anthracite to cannel, and include all the classes of so-called bituminous coals that are used for gas manufacture and coke-making.

The term "bituminous" is a misnomer, and probably arose from the coals softening with heat in the same way that bitumen does; but a consideration of the action of solvents upon them shows that those liquids which dissolve a true bitumen most readily have little or no effect on any of the coals, and it is clear that "resinoid" would be a more correct expression.

The differences which exist between the coals in this class are due to the proportion of the resin constituents present in the original vegetable deposits, which has largely conditioned the degree of degradation undergone by the humus bodies present, under the influence of time, temperature and pressure.

The brown coals and lignites, so abundant in certain parts of the world, are shown, by the strata in which they occur, to belong to the tertiary and sometimes even later geological periods. They have always been of great interest to the theorist, as forming a link between vegetation in the early stages of decay and true coal, being intermediate in composition between peat and those coals which contain the highest proportion of humus, such as some of the South Staffordshire coals. The lignites stand apart from true coals by the large amount of hygroscopic water they hold, and which cannot be got rid of by air-drying, and this, together with the large amount of oxygen they contain, makes this class of very poor fuel value as compared with coals of the carboniferous period. These tertiary coals are perhaps the most widely distributed, being found all over the world, but in England they are comparatively rare, the chief deposit in this country being at Bovey on Dartmoor.

In making any comparison as to composition between coals it is necessary to eliminate the factors of moisture, nitrogen, ash and sulphur, which, although they are amongst the most important items in the commercial value of the coal, yet mask by their variation the ratio existing between the carbon, hydrogen and oxygen in the coal material, upon which its classification most largely depends.

The analysis of carefully sampled coal when used in bulk for any manufacturing process is a necessity for proper control in working, but these analyses are often taken as representing the typical coal from some special colliery or district. As the coals in every seam, and even from different parts of the same seam, differ often to a considerable extent, unless the seam is specified, the analysis will be of little use save for the purpose for which it was made.

If coal from every seam in all the collieries could be systematically sampled and analysed, it would be a simply

invaluable work, and would throw an infinite amount of light upon the subject of the formation and composition of coal, but the analyses generally quoted tell one little else than that such a coal exists in the district.

In most of the coal-fields the seams represent different deposits of vegetation grown at periods which, from the strata separating them, may have been in some cases thousands of years apart. As the character of the atmosphere was rapidly changing so also would the character of the vegetation; and when one considers that one seam may be only a few hundred feet below the surface, and another three or four thousand, it is clear that the factors of temperature and pressure, as well as composition and time, must have varied to an enormous extent. It is small wonder therefore that the same colliery may possess a seam of gas coal and one of steam coal. In the same way, when a deposit has been of great area and different parts of it exposed to great variations in pressure and temperature during formation, it would be natural to expect differences in composition, and we see in the South Wales coal-field what must have been deposits of the same period changing from a bituminous coal in the east of the field to steam coal near the centre, and anthracite in the west.

It is perfectly clear that to collect the analyses of coal from one field, and to average them and take the mean result as giving the characteristics of the particular district, must give an utterly wrong impression unless seams of the same nature only are taken.

The use to which a coal is put often influences the way in which it is classified in our minds, so that if a North Country coal be spoken of to a gas manager, he at once thinks of the gas-making coals of his favourite Durham seams, whilst to the captain of a tramp steamer, North Country coal suggests the northern steam coals.

These considerations have made any geographical classi-

fication of coal difficult and misleading, as although certain kinds of coal form very often the chief bulk of coal exported from a given district, yet they by no means represent all the coals raised in that area.

When we come to classify coals on the basis of their chemical composition, we are met by the trouble of differences in results owing to variations in the methods of analysis employed, and in the fact that the ash, moisture and other traces present often mask the true proportion of the carbon, hydrogen and oxygen that form the true coal substance. The latter trouble can be got over by calculating the results of an ultimate analysis to a basis of carbon, hydrogen and oxygen only, whilst the former limits the number of usable analyses to those made by reliable analysts.

Certain coals on being analysed differ so widely in the proportions of their constituent elements that there can be no difficulty in distinguishing between an anthracite and a cannel, a lignite and a steam coal, but when one comes to differentiate between the representatives of the great class of so-called bituminous coals, it is at once found that difficulties arise, as one kind of coal merges by almost imperceptible alterations in composition into another coal, the characteristics of which stamp it as belonging to a different class. There are no hard and fast lines of demarcation between the various classes, no matter what the basis of the classification may be.

The earlier attempts at classification were mostly on the lines of the coking power and conditions of burning, the French arrangement of five classes being probably the best—

1. Poor coal, with long flame, non-coking.
2. Gas coal, long flame, poor coke.
3. Rich coal, shorter flame, fair coke.
4. Coking coal, short flame, best coke.
5. Anthracites and steam coal, little or no flame, non-coking.

When Regnault, in 1837, introduced the idea of using the ultimate analysis of the coal substance as a basis for classification, he realised that the proportion of oxygen present in a coal had an important bearing upon its properties and behaviour, whilst in 1873 Gruner attempted to improve upon the earlier classifications by defining the limits of the carbon, hydrogen and oxygen in the above arrangement, together with the yield of coke. This classification has been mentioned already in the first chapter, but is so important that it is reproduced here in its entirety (see Table on page 44).

This table was strongly criticised by Schondorff and later by Muck, who showed that with certain classes of coals it failed to bring out characteristic differences in property, whilst two very dissimilar coals might be classified together. Later, Fleck proposed a classification based upon the idea that all the oxygen in the coal was in combination with hydrogen, and that the proportion of the latter so combined was lost as a heat- and gas-yielding factor, whilst the excess of hydrogen over and above that needed by the oxygen was available hydrogen, and that the character of the coal was governed by the relation between the amounts of combined and available hydrogen. This classification also received severe criticism, and is, of course, based upon a fallacy that has given more trouble in the calorific valuation of coals than any other, and that is in supposing that all the oxygen in the coal is in direct combination with hydrogen.

Other attempts have been made to classify coals according to the volatile matter and fixed carbon yielded by a proximate analysis, this doing away with the more laborious ultimate analysis, such classifications being those introduced by Hilt, and more recently in America by Frazer.

Parr also has proposed to classify coals by the ratio of the volatile carbon to the total carbon, whilst Campbell

Classes or Types of Coal properly so called.	Per cent. Coke to Pure Coal.	Composition per cent.			Nature and Appearance of Coke.	Calorific Power.	Industrial Calorific Power. Water at 0°. Vaporised at 100 °per kilo of Pure Coal burnt, in Kilograms.
		Carbon.	Hydrogen.	Oxygen.			
1. Dry coals with long flame . . .	55 to 66	75 to 80	4·5 to 5·5	15·0 to 19·5	Powdery or slightly coked.	8000 to 8500	6·7 to 7·5
2. Fat coals with long flame (gas coals) .	60 to 68	80 to 85	5·0 to 5·8	10·0 to 14·2	Completely agglomerated, oftener caked but porous	8500 to 8800	7·6 to 8·3
3. Fat coals properly so called ("blacksmith coals") . . .	68 to 74	84 to 89	5·0 to 5·5	5·5 to 11·0	Caked, and more or less puffy	8800 to 9300	8·4 to 9·2
4. Fat coals with short flame (coking coals) .	74 to 82	89 to 91	4·5 to 5·5	5·5 to 6·5	Coked, compact	9300 to 9600	9·2 to 10
5. Lean coals or anthracite	82 to 90	90 to 93	4·0 to 4·5	3·0 to 5·5	Slightly coked, oftener powdery	9200 to 9500	9·0 to 9·5

proposes to use the ratio of the carbon to the hydrogen for the same purpose.

The latest classification is that of C. A. Seyler, who brings his great knowledge of the Welsh coals to bear upon the subject, and in the first instance utilises the percentage of carbon for coals containing less than 84 per cent. of carbon, whilst when the carbon exceeds 84 per cent. he finds that it is the percentage of hydrogen that conditions the character of the coal.

The coals below 84 per cent. of carbon are the lignites and brown coals, which he classes in three groups, and arranges the other coals in five main groups—

	Hydrogen per cent.	Approximate volatile matter per cent
Anthracite genus . .	up to 4	up to 10
Carbonaceous genus. .	4 to 4·5	10 to 16
Semi-bituminous genus .	4·5 to 5	16 to 24
Bituminous genus . .	5 to 5·8	over 24
Per-bituminous genus .	5·8 and over	..

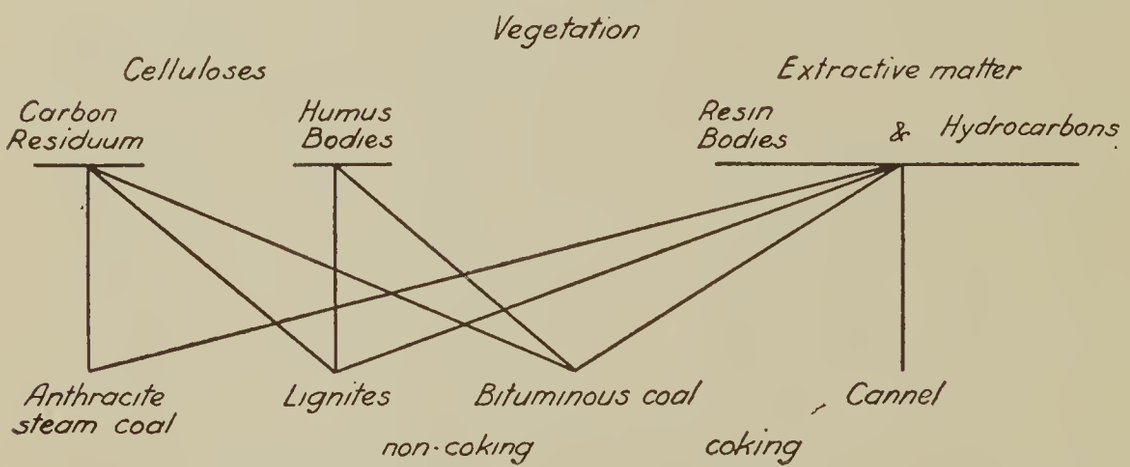
No stress, however, is laid on the volatile matter as a factor in the classification. These groups are then subdivided again into meta-, para-, and ortho-groups, and a very complete, although slightly complicated, tabulation of the coals is obtained.

In all such classifications, however, there is the weak point that none of them take the carbon, hydrogen and oxygen as anything but constituents of the coal substance, missing the fact that there are two sets of bodies each containing carbon, hydrogen and oxygen, and that it is the ratio of these two bodies to each other, and not the ratio of the constituents to each other, that must govern the properties and classification of the coal.

In every coal the carbonaceous residue from the com-

pleted decomposition of humus bodies is present in large quantities, whilst the coking power is conditioned by the resin bodies, to the presence of which hydrogen is the best indicator, and for these reasons a classification such as Seyler's must approximate more nearly to the truth than most of the others.

I have shown that coal is an agglomerate of the carbon residuum of humus bodies with humus in various stages of degradation, resin bodies and hydrocarbons derived from them, and if we desired to represent its formation diagrammatically, it might be done somewhat as follows—



and the coking power of the coal will depend upon whether the resin bodies and hydrocarbons preponderate, in which case it cokes ; or whether the humus bodies and residuum are in excess, in which case it is a non-coking coal.

The composition of the coal constituent has been seen to approximate to—

Residuum. A	Humus bodies. B		Resin bodies. C	Hydrocarbons. D
Carbon	Carbon	62	79	96·0
	Hydrogen	5	11	4·0
	Oxygen	33	10	0·0

With an equal mixture of these constituents there would be—

$$A+B+C+D = \left\{\begin{array}{ll}\text{Carbon} & 84{\cdot}3\\ \text{Hydrogen} & 5{\cdot}1\\ \text{Oxygen} & 10{\cdot}6\end{array}\right\} = \left\{\begin{array}{l}84{\cdot}6\\ 5{\cdot}2\\ 10{\cdot}2\end{array}\right\} \begin{array}{c}\text{A}\\ \text{Nottingham}\\ \text{Coal,}\end{array}$$

which would be Gruner's class 2—fat gas coal.

If, however, the humus is in excess the result would be a non-coking coal, such as

$$A+2B+C+D = \left\{\begin{array}{ll}\text{Carbon} & 79{\cdot}8\\ \text{Hydrogen} & 5{\cdot}0\\ \text{Oxygen} & 15{\cdot}2\end{array}\right\} = \left\{\begin{array}{l}79{\cdot}7\\ 5{\cdot}1\\ 15{\cdot}2\end{array}\right\} \begin{array}{c}\text{A South}\\ \text{Staffordshire}\\ \text{Coal.}\end{array}$$

If, however, the humus bodies are reduced, there is obtained

$$2A+B+2C+2D = \left\{\begin{array}{ll}\text{Carbon} & 87{\cdot}4\\ \text{Hydrogen} & 5{\cdot}0\\ \text{Oxygen} & 7{\cdot}6\end{array}\right\} = \left\{\begin{array}{l}87{\cdot}8\\ 5{\cdot}0\\ 7{\cdot}2\end{array}\right\} \begin{array}{c}\text{Derbyshire}\\ \text{Coal,}\\ \text{Monkswood,}\end{array}$$

corresponding to Gruner's gas and furnace coal.

In the true coking coals the percentage of humus has still further decreased, and there is obtained

$$3A+B+3C+3D = \left\{\begin{array}{ll}\text{Carbon} & 88{\cdot}8\\ \text{Hydrogen} & 5{\cdot}1\\ \text{Oxygen} & 6{\cdot}1\end{array}\right\} = \left\{\begin{array}{l}88{\cdot}59\\ 5{\cdot}26\\ 5{\cdot}85\end{array}\right\} \begin{array}{c}\text{South Wales}\\ \text{Coking}\\ \text{Coal.}\end{array}$$

In the anthracites and steam coals the humus has practically disappeared, and steam coal can be represented by

$$3A+2C+D = \left\{\begin{array}{ll}\text{Carbon} & 92{\cdot}3\\ \text{Hydrogen} & 4{\cdot}3\\ \text{Oxygen} & 3{\cdot}4\end{array}\right\} = \left\{\begin{array}{l}92{\cdot}4\\ 4{\cdot}3\\ 3{\cdot}3\end{array}\right\} \begin{array}{c}\text{Merthyr}\\ \text{Steam}\\ \text{Coal;}\end{array}$$

and anthracite as

$$5A+2C = \left\{\begin{array}{ll}\text{Carbon} & 94\,3\\ \text{Hydrogen} & 3{\cdot}1\\ \text{Oxygen} & 2{\cdot}6\end{array}\right\} = \left\{\begin{array}{l}94{\cdot}27\\ 3{\cdot}40\\ 2{\cdot}33\end{array}\right\} \begin{array}{c}\text{Neath}\\ \text{Anthracite.}\end{array}$$

It would be, of course, absurd to do more than point out that taken in these proportions the coal constituents do

correspond to the composition of well-known coals, and also correspond to the physical and coking properties of coals as classified by Gruner, whilst between these simple ratios the composition of one coal merges into another by such imperceptible degrees that no line can be drawn between the classes that shall be true for every case.

It is possible to obtain from these ratios an idea of the probable percentages of the coal substances present in the various classes of Gruner :—

	Carbon Residuum.	Humus Bodies.	Resin Bodies.	Hydro-carbons.
I. Flaming, A+2B+C+D .	20·0	40·0	20·0	20·0
II. Fat gas, A+B+C+D .	25·0	25·0	25·0	25·0
III. Furnace, 2A+B+2C+2D	28·6	14·2	28·6	28·6
IV. Coking, 3A+B+3C+3D	30·0	10·0	30·0	30·0
V. Steam, 3A+2C+D . .	50·0	...	33·4	16·6
VI. Anthracite, 5A+2C .	71·4	...	28·6	...

Which shows the gradual increase in the carbon residue and also the fact that resin bodies and hydrocarbons have to be present in the proportion of at least 50 per cent. for coal to have the property of coking.

The great class of coals of the tertiary and later periods vary amongst themselves even more in composition than the bituminous class. Although but little attention has been paid to them in this country, owing to the fact that there are only very small and unimportant deposits of them, the chief one being the Devon deposit at Bovey, yet on the Continent they attain considerable importance, the lignite and brown coal deposits being of enormous extent and playing an important part in the fuel assets of the various countries, whilst, as we go south into tropical countries, the true coals become still rarer, and most of the carbonaceous deposits are lignitic in their character. Some of these bodies are nearly akin to peat, some little more than

fossilised wood, whilst others again are so near to coal that, as far as the ratios of carbon, hydrogen, and oxygen go, they might be mistaken for a bad sample from the Staffordshire 10-yard seam.

	Carbon.	Hydrogen.	Oxygen.
Abbeville peat . .	60·89	6·21	32·90
Austrian lignite . .	61·01	6·06	32·93
Italian lignite . .	79·01	5·76	15·23
Staffordshire coal (bad)	79·70	5·37	14·93

Between these limits many possible ratios of the elements are to be found.

There is one characteristic, however, by which all members of this class may be distinguished ; that is, that they are so little removed from the wood from which they were formed that they still retain the hygroscopic property that is to be found with all wood. Lignites may contain anything up to 40 per cent. of water, which on air-drying may be reduced to 15 to 20 per cent., but can be brought below this only by drying for a long time at 105° C. (221° F.) ; and when the dried material is again exposed to moist air, it reabsorbs the moisture so driven out ; this, of course, seriously reducing its value as a fuel.

In the lignites the humus bodies have undergone the minimum of degradation, and the ratio of carbon residue to humus is the smallest found in any coal. If we take the coal substance of the English lignite, it corresponds to 5B+A+C =

Carbon . .	69·9	69·53
Hydrogen . .	5·1	5·91
Oxygen . .	25·0	24·56

} Bovey lignite.

It is clear that the composition of a coal must have an enormous influence on its calorific value. Even as early as 1844 Professor W. R. Johnson analysed all the kinds of

coal then used by the American Navy and determined their evaporating power. Since then the importance of calorific value has been thoroughly recognised, and in the middle of the last century the work of Favre and Silbermann, of Morin and Tresca, of Scheurer-Kestner and of Meunier-Dolffus, all helped to put the testing of coal for heating value on a sound basis.

The heat generated by the combustion of the more commonly occurring combustible elements and compounds when burnt in oxygen was determined by Favre and Silbermann, Dulong and Petit, Thomson and others. Their figures have been taken as a basis from which the calorific value of a coal is often calculated from its ultimate analysis, but as this introduces several serious errors, and as a direct determination by experiment in any of the bomb calorimeters is easier and quicker to make than a good ultimate analysis, the more accurate determination is rapidly taking the place of calculated results.

Of late years an enormous amount of work has been done on the calorific value of coals, by Bunte, St Claire Deville, Mahler, and, quite recently, by Constam and Kolbe. These later observers, after a long investigation of the heat values of the more important types of continental coal, came to the conclusion that coals which contain about 18 to 32 per cent. of volatile matter have, together with the anthracites, the highest heat value. On extending their researches to some English coals, however, they found exceptions to this rule, and consider that the exceptions are due to the fact that the chemical composition and the heat of combustion of the volatile constituents are not always functions of their amount.

Now it is clear that if coal consists of an agglomerate of several bodies of different calorific value, the proportion of these bodies present, and not the amount of fixed carbon or volatile matter, will determine the heat value of the coal.

If we take the calorific value of the coal constituents we obtain—

	Calories.
A. Carbon residuum . . .	8137
B. Humus bodies . . .	6485
C. Resin bodies . . .	9126·5
D. Hydrocarbons . . .	8836

On calculating from these factors the calorific value of the various classes of coal, we have—

	Calories.	B.Th.U.
Lignite, Bovey, A+5B+C . . .	7,098·3	12,758·9
A Staffordshire coal, A+2B+C+D .	7,813·9	14,065
A Nottingham coal, A+B+C+D . .	8,146	14,662
A Derbyshire coal, 2A+B+2C+2D .	8,383·4	15,090
Coking coal, 3A+B+3C+3D . .	8,478·3	15,261
Steam coal, 3A+2C+D	8,583·3	15,489·6
Anthracite, 5A+2C	8,419	15,154·2

These figures agree with what we know of the calorific values of such coals, and show clearly that it is the low heat value of the humus bodies which lowers the thermal value of the lignites and coals most nearly akin to them. The maximum heating value is attained only when the humus is entirely eliminated, as is the case with steam coal and anthracite.

As we have seen, an analysis of a true cannel, like the old Scotch boghead cannel or Torbane Hill mineral, suggests that it consists of resin bodies only ; and this is borne out by its calorific value, after deduction of the ash present, this being 9134 calories or 16,441·2 B.Th.U.

The calorific values calculated as above will be a little low for the lignite and first four classes of bituminous coals, as the calorific value of the humus is taken, and amongst the coal bodies there will be, undoubtedly, products of its degradation intermediate between the humus and the

carbon residuum, and therefore having a calorific value higher than that of the humus.

Another very important point brought out by this consideration of the way in which the calorific value of coal is built up from the calorific values of its constituents is that it brings out in a striking way the cause of the discrepancies always found between the heating value of a coal of high oxygen content as calculated and as determined by the bomb calorimeter.

A sample of artificially prepared humus was analysed, and its calorific value calculated by the formula—

$$Q = \frac{1}{100}(8137\ C + 34{,}500\ (H - \frac{(O + N) - 1}{8}),$$

which gave a calorific value of 5392 calories. Its calorific value was then determined in the Mahler bomb, which gave 6485 calories, or an increase of 16·8 per cent. in its thermal value.

It is well known that if a coal be carefully analysed, and its thermal value is then determined in a bomb calorimeter and compared with the thermal value as calculated from the most generally accepted formula from the analysis, the results will be in very fair accord as long as one deals with an anthracite or steam coal low in oxygen content, but that directly there is any large amount of oxygen, and therefore high volatile matter in the coal, the value as determined rises rapidly above the calculated value.

In the calculation it is presumed that all the hydrogen goes in combination with oxygen to form water, so that its heating value is lost to the coal, whilst we know that if coal be decomposed we obtain large volumes of free hydrogen, and that unless the temperature of decomposition is very low but little water is formed, and the tar contains most of the oxygen as oxygenated hydrocarbons. That is to say, the complex character of the oxygen compounds in the

coal and the way in which they break up render the calculation of thermal value too low, and it is evident that it is the humus bodies in the coal substance which give rise to this trouble.

All classes of bituminous coals and lignites will be affected by it, and the higher the percentage of oxygen the greater will be the difference, so that if the calculation of the thermal value of the humus be 16·8 per cent. too low, then the various classes of coal would be affected to the following extent—

(Gruner).

		Oxygen.	Calculation too low.
Class I.	Flaming coals . .	13–18·5	6·7 per cent.
,, II.	Fat gas coals . . .	10–13·2	4·0 ,,
,, III.	Furnace coals . .	5·5–10	2·4 ,,
,, IV.	Coking coals . . .	4·5–5·5	1·6 ,,
,, V.	Steam coals } Anthracite }	3·0–4·3	agrees

Brame and Cowan made careful analyses of five samples of dried coal in duplicate, the mean of two analyses of each being taken. Three determinations of the calorific value of each coal in the Mahler bomb were then made, and these being in close agreement, the mean of the three tests was taken in each case.

Analysis of Coals (Dry) and Calorific Value.

Coal.	Carbon.	Hydrogen.	Sulphur.	Ash.	Oxygen and Nitrogen.	Calorific Values.		Calculated value too low.
						Calculated.	Determined.	
A	90·09	3·85	0·77	1·68	3·61	8567	8629	0·7
B	81·02	3·23	0·64	9·50	5·61	7527	7713	2·4
C	87·79	4·09	0·59	3·14	4·39	8425	8617	2·2
D	84·07	4·51	0·68	5·69	5·04	8241	8394·5	1·8
E	78·29	4·76	1·48	4·90	10·57	7638	8026·5	4·8

If the true coal substance be calculated as free from ash these figures are in very fair agreement with the calculated corrections as given in the previous table.

The formula used for the above calculations of calorific value was—

$$Q = \frac{1}{100}(8140\ C + 34{,}500\ H\ (\frac{(O + N) - 1}{8}) + 2220\ S).$$

These results confirm the conclusion that, as regards the heating value of coal, direct determination in the Mahler bomb is the only method that can be relied upon to give accurate results.

In 1908 Constam and Kolbe made a long investigation on the relation existing between the volatile matter in Continental coals and their calorific value, in which they came to the conclusion that coals containing from 18 to 22 per cent. of volatile matter and anthracite had the highest calorific value, but it was found that samples of English coals did not conform to this law. To explain the difference eight typical samples of English coals were experimented with, and as a check a sample of Kinneil coal, which had been used on a large scale at the Zurich gasworks, was also taken.

The results, which as regards composition, etc., of the coal will be given in Chapter VI. in a tabulated form, show that although the volatile matter, obtained by deducting the coke yield from the ash and moisture-free coal substance, was practically equal in the Lancashire Trencherbone, Nottingham best hard, and Kinneil coals, yet the calorific values varied by over 500 B.Th.U., whilst with the Hutton seam and Barnsley coals, although the volatile matter was nearly the same, the thermal values differed by about 900 B.Th.U. The conclusion was arrived at that these differences were due to the different composition and heating value of the volatile constituents from these coals.

I have already pointed out that the factor which governs the calorific value of a coal is the percentage of humus body present in it, as this, having a far lower heating value than any of the other constituents, drags down the calorific value.

The composition of the humus and resin bodies is perfectly distinctive—

	Humus.	Resinic.
Carbon . . .	63	79
Hydrogen . . .	5	10
Oxygen . . .	32	11

And the whole of the oxygen present in the coal is due to these two classes of compounds. In the resin bodies there is a difference of only 1 per cent. between the oxygen and hydrogen present, so that for all practical purposes they may be taken as being equal, whilst in the humus bodies there is 32 per cent. of oxygen to 5 of hydrogen.

Hydrogen is also present in the hydrocarbons of the coal, but these latter are derived from the resin bodies and have a calorific value but little below them, so that the excess of oxygen in a coal over the hydrogen, by giving an indication of the amount of humus, should give the order in which coals stand to each other in regard to their calorific values.

No better set of figures could be chosen to test the truth of this theory than the figures given in Constam and Kolbe's research on typical English coals, because, when viewed from the ordinary standpoint, the figures are a mass of anomalies, but we know that Professor Constam's work is absolutely reliable, and that no figure trimming has taken place to make them fit any preconceived theory.

Taking the coals in the order in which Constam and Kolbe give them, we obtain the following results for the oxygen minus hydrogen :—

	Oxygen.	Hydrogen.	Resultant.	Order in Calorific Value.
I. Nottingham, bright coal	10·20	− 5·30 =	4·90	IX.
II. Lancashire, Trencherbone	7·05	− 5·38 =	1·67	V.
III. Nottingham, best hard	9.24	− 4·97 =	4·27	VIII.
IV. Kinneil	8·23[1]	− 5·55 =	2·68	VI.
V. Durham, Low Main	5·66	− 5·48 =	0·18	IV.
VI. Durham, Hutton	3·70	− 5·46 =	− 1·76	II.
VII. Yorkshire, Barnsley	7·92	− 4·82 =	3·10	VII.
VIII. Durham, Ballarat	4·22	− 4·95 =	− 0·73	III.
IX. Welsh, Nixon's Navigation	2·58	− 4·72 =	− 2·14	I.

[1] The nitrogen in the Kinneil coal was not determined, but I have an analysis with 1·01 as the amount present, so have deducted it from the oxygen.

Coals in Order of Oxygen − Hydrogen.

	Calorific Values, B.Th.U. (determined).	
	Gross.	Net.
I. Nixon's Navigation	15,730	15,271
II. Durham, Hutton	15,766	15,235
III. Durham, Ballarat	15,590	15,109
IV. Durham, Low Main	15,392	14,859
V. Lancashire, Trencherbone	15,124	14,602
VI. Kinneil	15,032	14,494
VII. Nottingham, best hard	14,555	14,072
VIII. Nottingham, bright	14,522	13,912

This method of fixing the calorific position of an anthracite or a steam coal would not answer in all cases, as the humus has all been eliminated from them and only the residuum is left to represent it, but the above table shows that it will put the bituminous coals into their true calorific order.

It also makes clear the anomalies which at the outset of their research troubled Constam and Kolbe, *i.e.* why coals containing the same proportion of volatile matter

should differ so widely in calorific value. The reason is that both humus and resin bodies go to make up the volatile matter, and the proportion in which they are present governs the calorific value, not the total amount of volatile matter.

The Trencherbone, Nottingham hard, and Kinneil coals all had nearly the same percentage of volatile matter, but in the Trencherbone and Kinneil it was largely resin bodies, whilst in the Nottingham coal it was mostly humus, so that the latter had a calorific value 500 B.Th.U. less than the former coals. In the same way, the Durham Hutton seam and the Yorkshire Barnsley are fairly close in volatile matter, but the former is rich in resonoid bodies, the latter in humus bodies, hence the difference of 900 B.Th.U.

The English coal-fields are usually divided into seven areas or basins, the coal in which probably has a total area of not less than 2700 square miles, whilst the country over which they are spread is, of course, enormously greater.

1. The Newcastle field, on the eastern side of Durham and Northumberland.
2. The Cumberland field, in the north-west of the county.
3. The Lancashire, Cheshire, and Flintshire field.
4. The Yorkshire, Derbyshire, and Nottingham field.
5. The Midland field.
6. The South Wales field.
7. The South of England field, which includes the Bristol, Somerset, Forest of Dean, and Kent areas.

The Newcastle field provides the largest amount of the coal used for gas-making wherever water carriage can be utilised. The coals of this basin are very variable—in some districts being hard, free-burning, and suitable for steam purposes, whilst others give some of the most useful gas coals (which could not be nearly so well adapted for steam raising), and excellent coking coal and good domestic coal occur in the same district.

In the Cumberland field, in the Whitehaven district, good steam and coking coal is obtained.

Nearly every class of coal is represented in the Yorkshire district, the coal of South Yorkshire being best suited for coking purposes, whilst in some parts of the West Riding the coal falls into the non-coking classes.

The Lancashire coal includes the celebrated Wigan seams, from which some of the richest gas coals in the country have been obtained. In the St Helens district a good deal of the coal is available for steam and furnace purposes. The Burnley field also yields, in various seams, coals useful for household and mnaufacturing purposes and for steam raising.

North Staffordshire yields some good gas and coking coals, but they are mostly more fitted for household and manufacturing purposes. In South Staffordshire, together with coals of this latter class, occurs the celebrated ten-yard seam, parts of which approach to Class I. of Gruner's classification, and are probably the nearest of the true coals akin to the lignites. Other parts of the seam, however, give a thoroughly good bituminous coal.

The coals of the Derbyshire district are mostly used for steam, house, and manufacturing purposes.

In the Nottingham, Leicester, and Warwickshire districts the coals are all of the bituminous type. Coming south to the Forest of Dean coal-field, some excellent seams of household, manufacturing, and steam coals are to be found, and this area is supposed to represent some of the Welsh seams.

There is also included in the South of England coal-field the Somerset area, which consists of bituminous coals, useful for coking, household, gas, and manufacturing purposes, and, with the exception that they contain rather more ash, are not very far behind the Durham gas coals.

Another area at Bristol yields fair coking, household, and manufacturing coal. These measures are supposed to run

under the South of England, giving the Kent area, and under the Channel, to the Pas de Calais coal-fields, and probably also some of the Belgian fields.

The South Wales coal-field stands alone in interest, giving in the eastern portion the bituminous coals, as found in the Taff and Rhondda valleys. From there to the Vale of Neath the true steam coals occur, beyond that the anthracites; and indeed in this area almost every class of coal, bituminous, semi-bituminous, coking, steam coals, and anthracite are represented.

Coal occurs in large quantities in Scotland, and to a small extent in Ireland.

In considering the distribution of coal, a point of the greatest interest is how our coal resources compare with those of other countries, and also the rate at which they are being consumed. It must be remembered that the commercial supremacy of England is dependent to a very great extent upon her coal supplies, which during the last century made this country the centre of manufacturing industries, and that, when once the coal supply fails, commerce is bound to follow the cheapest manufacturing market.

Not only has America the largest store of coal in the world, but it has the further advantage that the amount that has been mined is comparatively small. It is only of late years that the output of coal has been in proportion to the magnitude of her coal-fields, but in the last year of the past century she deprived England of her position as the world's greatest producer, and now is easily first, raising at least a third more than is done in the United Kingdom.

Leaving America to look after her own vast interests, let us see how the ratio between capital and expenditure compares for the chief European Powers, taking them in order of coal production—

	Production per annum. Tons.	Total coal. Millions of tons.
Great Britain . .	236,130,000	140,000
Germany . . .	119,350,000	150,000
France . . .	34,780,000	17,000
Belgium . . .	21,500,000	16,000
Russia . . .	17,120,000	20,000

Such figures can be only the merest approximation, but if they are of any value at all they mean that we are the spendthrift of Europe, and that our supremacy is at the cost of such capital expenditure that, unless we take the position seriously and do everything in our power to retrench by economising much of the fuel now wasted, before many generations have passed we must lose our priority amongst the European nations.

At the present rate of use, our coal-fields would be exhausted in a little over 600 years, which seems at first sight to be a fairly comfortable reflection, but it is clear that the use of coal will go on increasing until shortage and consequent rise in price checks the demand. Although the increase in the demand may not be in the proportion that has characterised the past ten years, yet it would be absolute folly to expect it to remain at the present figure, unless drastic steps are taken to prevent waste. Moreover, it is manifest that the cream of the coal supply has been utilised, and that a very large proportion of the existing supply is at greater depths and in thinner seams than that which has been used in the past, and must of necessity therefore entail much greater expense in winning. So that it is not the remaining amount of coal which governs the question of relative power, but the price at which that coal can be commercially used.

Although it may be possible to prove by statistics that our coal supply will last for 600 years, it is quite within the range of possibility that, if the increased consumption continues, a period may come within a very few generations when the cost of coal has so risen as to enable foreign markets

to obtain coal at a cheaper rate than our own supply. Even at the present time, a few shillings' increase in the price of coal would give a tendency in this direction.

The Royal Commission on Coal Supplies which reported on the resources of our coal-fields in 1905 went fully into the question of the amount of coal remaining and its probable duration, and estimated that the available quantity of coal in the proved coal-fields of the United Kingdom is roughly 100,000 million tons, together with a probable 40,000 million tons in the unproved fields. The amount of coal now raised annually amounts to about 250 million tons, and for the last thirty years the average increase has been at the rate of $2\frac{1}{2}$ per cent. per annum, whilst the amount exported has increased at the rate of $4\frac{1}{2}$ per cent. per annum. They, however, consider that it is extremely improbable that this increase will continue. They are of opinion that the rate of increase will slow down, and will be followed by a period of stationary output and then a gradual decrease; but they admit that the outlook is serious, and go fully into the possible economies which could be arrived at in the working and consumption of coal.

The coal raised is utilised for various purposes, which may be represented in percentages as follows—

	Per cent.
Factories	22·97
Domestic	13·87
Iron and steel manufacture	12·17
Mines	7·80
Gasworks	6·50
Railways	5·53
Potteries, brick-works, glass-works, and chemical-works	2·16
Metal and minerals	·43
Coasting steamers	·87
Steamers over seas	7·25
Exported	20·35

Bearing in mind the distribution so shown of the consumption of fuel, it will be well to now glance at the directions in which economy is possible, and the extent to which such economies would reduce the total consumption.

England suffers to a great extent from the stolid adherence to old ideas and methods which have served her well in the past, and which she hesitates to throw aside; and many commercial firms still cling to the procedure of their founders until they find they can no longer hold their own with the products of more up-to-date processes. Trade once lost is hard to regain in these days of keen competition. In America and Germany, directly an improvement proves its worth, no hesitation is shown in scrapping obsolete machinery or relegating wasteful processes to oblivion. Although in certain branches of trade we are beginning to adopt progressive methods, much remains to be done, and in no direction is there greater scope for improvement than in the production of power and generation of heat.

In his evidence before the Royal Commission, Dr G. Beilby gave the following excellent summary of the possible economics that might be obtained in the various uses to which coal is put—

	Consumption. Millions of Tons.	Saving in Millions of Tons.	Means of Economy.
Railways	12–14	5– 7	Gas generator and engine; electric motor & traction.
Stations	6–8	...	
Factories	40–45	20–30	
Mines	10–12	5– 7	Gas engine and recovery ovens.
Blasting Furnaces	16–18	2– 3	
Iron and Steel	10–12	2– 3	Gas generator and coke.
Other Metals	1–2	...	
Brick-works, Potteries, Glass, and China	4–6	1– 2	
Gasworks	14–15	...	Gas cooking and heating, briquettes and coke.
Domestic purposes	30–36	5–8	
	143–168	40–60	

This shows that there is more coal used for power production than for anything else, and out of the seventy million tons used for this purpose practically one-half could be saved if wasteful and inefficient steam-engines were replaced by modern types.

The internal combustion gas-engine and gas producer have made slow progress as compared with the steam boiler and turbine, the great advantage of the latter being that it can be used in much larger units, whilst the gas-engine has not been a very great success in units over 1000 h.p. The result has been that in large central stations for the generation of electricity the steam turbine has advanced with great rapidity.

The gas-engine, however, is steadily progressing, and will every day occupy a more important position in total power production. It is not at all impossible that this advance in power production may lead to the diminution in the quantity of coal annually raised that the Commission of 1905 hoped for or thought probable. The use of gas for heating and cooking purposes also has diverted a certain proportion of coal from the domestic fireplace, where its consumption was extremely wasteful, and deleterious to the atmosphere and air of large towns, and has enabled the gas industry to supply more and more gas for heating purposes, which is a distinct advantage from the point of view of economy in coal and improvement in atmospheric conditions.

CHAPTER III

THE FORM OF RETORTS USED IN GAS MANUFACTURE

The early work of Murdoch—Apparatus for the distillation of coal—Murdoch's retorts—Clegg's rotary retort—Disadvantages of iron retorts—Fireclay retorts—Leakage with clay retorts—Scurfing—Early inclined retorts—Early vertical retort—Bueb's intermittent vertical retort—Dessau vertical retorts—Woodall-Duckham continuous vertical retorts—Glover-Young systems—Glover-West continuous vertical retorts—Carbonisation in bulk—Chamber carbonisation—Fully charged horizontal retorts—Glover's chamber retorts—Yield of gas from the various systems—Fuel consumption in the various systems—Advantages of the continuous vertical retort

The practical utilisation of coal gas for the production of light and heat was due undoubtedly to William Murdoch, a young Scotch engineer, who in 1779 went to Cornwall in order to introduce the engines and pumping machinery of Messrs Boulton and Watt in the tin-mines of the district, many of which suffered from the influx of water. Making his headquarters in the small market town of Redruth, he employed such spare time as he had in trying a number of experiments upon various points that had suggested themselves to him in his earlier years, and amongst which was the production of illuminating gas from coal.

The fact that inflammable gas could be obtained by the distillation of coal had been recognised at least a hundred years before Murdoch's experiments, but it was he who showed first how coal gas could be made a valuable aid to civilisation.

So much has been said as to the part he played in the discovery that his own account of his experiments and claims,

published in *Nicholson's Journal* in 1808, is of the greatest interest.

"It is now nearly sixteen years since, in the course of experiments I was making at Redruth, in Cornwall, upon the quantities and qualities of different kinds of gases produced by the distillation from different mineral and vegetable substances, I was induced, by some observations I had previously made upon the burning of coal, to try the combustible property of the gases produced from it, as well as from peat, wood and other inflammable substances; and being struck with the great quantities of gas which they afforded, as well as with the brilliancy of the light and the facility of its production, I instituted several experiments with the view of ascertaining the cost at which it might be obtained, compared with that of equal quantities of light yielded by oils and tallow.

"My apparatus consisted of an iron retort, with tinned copper and iron tubes, through which the gas was conducted to a considerable distance; and there, as well as at intermediate points, was burned through apertures of varied forms and dimensions. The experiments were made upon coal of different qualities which I procured from distant parts of the kingdom for the purpose of ascertaining which would give the most economical results. The gas was also washed with water, and other means were employed to purify it.

"In the year 1798 I removed from Cornwall to Messrs Boulton, Watt and Co.'s works for the manufacturing of steam engines at the Soho Foundry, where I constructed an apparatus upon a larger scale, which during many successive nights was applied to the lighting of their principal building, and various new methods were practised of washing and purifying the gas.

"These experiments were continued with some interruption until the peace of 1802, when a public display of this

light was made by me in the illumination of Mr Boulton's manufactory at Soho on this occasion.

"Since that period I have, under the sanction of Messrs Boulton, Watt and Co., extended the apparatus at Soho Foundry, so as to give light to all the principal shops, where it is in regular use, to the exclusion of all other artificial light.

"At the time I commenced my experiments I was certainly unacquainted with the circumstance of the gas from coal having been observed by others to be capable of combustion; but I am since informed that the current of gas escaping from Lord Dundonald's tar ovens had been frequently fired; and I find that Dr Clayton, in a paper in vol. xi. of *Transactions of the Royal Society*, so long ago as the year 1739, gave an account of some observations and experiments made by him, which clearly manifest his knowledge of the inflammable property of the gas, which he denominates the spirit of coals; but the idea of applying it as an economical substitute for oils and tallow does not appear to have occurred to this gentleman, and I believe I may, without presuming too much, claim both the first idea of applying and the first actual application of this gas to economical purposes."

When Murdoch first made coal gas at Redruth, the retort which he employed was simply a cylindrical iron pot, set, in the same way that a scullery copper is, over an open fire. It held a charge of 15 lbs. of coal, was closed at the top by an iron lid, and the gas was led off 3 or 4 inches below the lid by a horizontal pipe of iron. The trouble, however, of removing the coke after the carbonisation of the charge was so manifest and serious a drawback, that as early as 1802 he had adopted a horizontal cylindrical vessel, from which the charge could be raked out more easily, whilst the flue was so constructed that the flame surrounded the retort and then made its escape direct into the chimney. He seems to have tried several settings of this character, with retorts varying in size

from 1 foot to 20 inches in diameter, and from 3 feet to 7 feet in length.

At this period also he seems to have tried a cylindrical retort placed at an angle of about 45°, with a mouthpiece at each end to aid in charging and discharging. None of these earlier forms of retort were of any great size, the usual charge he employed being about 15 lbs. Soon after he reverted to the pot form, and in order to facilitate the discharging of the coal fitted into it an iron cage, which was put in before the coal charge, and which could be lifted out bodily by means of a small crane. In this he carbonised 15 cwt. of coal at a time. In this experiment he came upon a trouble which is common to every process of carbonisation in bulk. That is that the process of carbonisation proceeds rapidly at first, producing a layer of coke next to the heated surface, and this, being a bad conductor of heat, retards the process of carbonisation, owing to the slowness with which the heat is transmitted to the inner portion of the charge, whilst the gas evolved in the interior portion of the charge, having to pass through the heated coke, loses a large proportion of its illuminating power, in consequence of the breaking down of the rich hydrocarbons, with liberation of oxygen.

Before 1810 Murdoch had also discovered that in order to get the best gas yield a high temperature was necessary, and that if the coal is carbonised at too low a temperature the volume of tar produced was greatly increased, and the yield of gas reduced in a corresponding ratio. He also made a certain amount of progress in the setting of the retorts in the furnace, by making flues around the horizontal retorts, which would ensure as much as possible of the heat being utilised.

At this period the evils arising from submitting the gas to too long a travel through the incandescent coke seem to have been generally realised by other observers, and attempts began to be made to carbonise the coal in thin layers, so that

the gas should escape more freely and would not have to pass over any very great surface of heated carbonised material. A retort was patented by Clegg in 1815, which he termed a rotary retort, which consisted of shallow boxes attached to radial arms rotating on a central shaft. The coal was charged in at the cool side of the shallow circular retort into the trays, and in this place also the tray of coke could be removed. Carbonisation took place on the heated side of the retort, into which the radial arms carried the tray containing the new charge. Although several installations were erected, as might be expected they proved a failure; a fate which also befell his web retort, in which an endless chain carried the coal to be carbonised in a thin layer through the carbonisation chamber.

The advantages of a thin stratum of coal being fully recognised, Malam introduced wide oval retorts set in a horizontal position, the bottom only of which was charged with coal, and he further made an advance in the setting by placing five and six retorts in a bench heated by three fires.

By 1841 the form of retort used seems to have settled down to an oval, ⏛-shaped or circular retorts, five of which were placed horizontally in the same bed or setting. These retorts, being deteriorated rapidly by direct contact with the fire, were protected by fireclay shields or tiles.

In none of these earlier retorts, however, could any temperature beyond 800° C. (1472° F.) be employed, as otherwise the exterior became so acted upon that the retort had a life of only a few months. Even with the greatest care the life of a retort was seldom more than eight or nine months. Even when working at lower temperatures than those usually employed, it is found that great trouble is caused by what is known as the "growing" of iron, which takes place unless the greatest possible care is taken in the selection of the metal. This phenomenon is caused by the hydrocarbon gases permeating the metal and becoming decomposed there,

so leaving a deposit of carbon, which gradually forms a spongy mass. It is not an unusual thing for a 10-foot retort to increase two or three inches in length after a few months' working, from this cause.

Not only do the gases evolved render the iron spongy by penetration and decomposition, but the carbon shed off from decomposed gases and vapours like ethane and ethylene deposit on the heated surface of the crown of the retort. The action is at first slow, but as soon as an initial coating has formed, it proceeds with great rapidity, owing to the catalytic action its surface produces, with the result that deposits of retort carbon some inches in thickness are not uncommon. This highly adhesive coating not only interferes with the rate of passage of heat into the retort, but, having a different rate of expansion and contraction to that of the iron, when the retort is cooled down often leads to its cracking. The exterior of the retort, moreover, is attacked rapidly by the flue gases, and flakes off in masses of oxide and other compounds, whilst any pressing of temperature leads to distortion of the retort and displacement of the protecting tiles.

This trouble with the metal retorts led to attempts being made to introduce fireclay retorts. These met with such opposition that it was not until nearly the middle of the century that they became generally adopted. Before fireclay retorts became general, brick ovens were used in many places. The early ones were square and capable of containing about 4 to 5 cwt. of coal per charge, but later were altered to a flattened ⌓-shape and increased in size, so as to be capable of receiving a charge of 10 to 12 cwt. of coal. In these, carbonisation seems to have been vary rapid, as five hours is given as the time taken to carbonise the charge ; but the consumption of fuel was excessive, sometimes rising to 70 per cent. of the coke produced. This, however, was probably largely due to faulty construction of settings and furnace

and general flue arrangements. Their life, however, was four or five years, and they produced coke of a very good quality.

In the early fifties, fireclay retorts almost entirely displaced these ovens, and have ever since been adopted, their section being made much the same as with the old iron retorts.

A great deal of the early opposition to fireclay retorts was due undoubtedly to prejudice. They were adopted in Scotland for many years before they became used generally in England. The chief points urged against fireclay by its opponents were that, as its conducting power was only about one-tenth that of iron, the period of carbonisation would be increased to a serious extent, and that leakage would be excessive, owing to the porous nature of the baked clay. Moreover, in the early retorts the methods of manufacture, and in some cases the quality of the clay used, led to cracking and breakage, which increased the prejudice against them; but with the introduction of better clays into the manufacture and the admixture of a large proportion of burnt clay with the plastic clay, to prevent shrinkage in baking, these troubles mostly disappeared.

Lewis T. Wright made some tests upon the amount of gas lost by leakage with clay retorts under working conditions—

Retort.	Pressure of gas in tenths.	Condition of retort.	Loss of gas per foot super. of retort per 24 hours.
1	10	in use	2·46
1	5	after scurfing	7·10
2	10	in use	2·59
2	5		1·46
3	10	in use	3·20
3	5		1·53
4	10	recently scurfed after 18 months' use	13·6
4	5	,, ,,	6·8

This shows the important part played by deposited carbon in keeping the retorts gas-tight. As, however, the average pressure in the retorts would not exceed $\frac{3}{10}$ths, the conclusion is that the loss is not serious.

As can easily be imagined, the fifty years from the inception of the gas industry also saw great advances in the retort settings. These resulted in considerable fuel economy, so that by the early sixties the fuel consumption had settled down to about 20 per cent. of the coke produced. Up to this time most of the retorts had been what is termed " single-ended "—that is, closed at one end—and had only one mouthpiece ; but in the larger works double-ended retorts, with a mouthpiece at each extremity, soon began to displace these.

The advances which had been taking place both in the material of the retorts and in the settings had led to a general increase in the temperature of carbonisation employed, but even in the days of the iron retort it was found, as we have seen, that considerable trouble arose from a crust of dense carbon deposited on the inner surface of the crown of the retort, due to the effect of heat upon the escaping hydro-carbons, and when, with the introduction of fireclay retorts, the temperatures were raised, this became a very serious trouble, as it led to the retort having to be scurfed at frequent intervals. If this was done mechanically, as it generally was, great damage to the retort resulted. A slight improve-ment took place with the discovery that the deposit could be burnt off easily by causing a flow of air over the surface of the retort when heated and empty, which burnt off the carbon, and that a mixed steam and air blast could be used with even greater advantage for this purpose.

The trouble, however, was at one time so great that it appeared as if the limit of temperature had been reached ; but the discovery of the fact that pressure had an enormous influence in causing this deposit led to the introduction of the

exhauster to suck the gas away from the retort, and this, giving the possibility of working with little or no pressure in the retort, led to a great improvement in the amount of deposit formed, and also in the quality and quantity of the gas produced.

About 1885 Coze introduced the idea of placing the retort just at the angle of slip of the coal, so as to utilise gravity to aid in the charging and discharging, the charging being done from a hopper through the mouthpiece at the upper end of the retort, whilst, after the charge had been carbonised, the removal of a stop and the " tickling " of the charge caused it to slide out. This idea being adopted gradually, the inclined retort has played a very important part in gas manufacture during the past twenty years, and by the application of gas-firing and regenerative settings very high efficiency has been obtained from them.

The inclined retort, in reality, has proved the link between the horizontal retort and the new methods of carbonisation ; and it is curious to note that after a century of practically little or no advance in carbonising coal, the early years of the present century are marked by the same energy in the development of new processes that marked the introduction of the horizontal retort during the same period of the last century. The cause of this activity has been the reduction of candle power incidental to the almost universal adoption of the mantle for lighting purposes, which led to a lowering of the parliamentary standard.

At first, the gas manager attempted to increase the volume of gas obtained per ton of coal and bring its illuminating power down to the new standard by pressing the temperature at which the coal was undergoing carbonisation, but, for reasons already dealt with, this gave rise to such troubles that new methods were sought. This new era may be considered to have started with the inauguration of the vertical retort, in which, by utilising a large oval fireclay retort set on end,

and with a slight taper from bottom to top, much larger charges could be used than had been possible with the horizontal or inclined retorts, and in which also gravity was utilised to the full for charging and discharging.

The vertical retort dates back to 1828, when it was first introduced by John Brunton, who, finding that the gas could not escape freely from the lowest portions of the charge, and so created considerable pressure, put a perforated pipe in the centre of the charge, to afford an easy way of escape. Nothing more was heard of the process, so it is presumed it failed ; but at later dates attempts of the same kind were made by Lowe and Kirkham, and also by Scott.

After these early attempts nothing was done until Rowan, in 1885, patented the idea of carbonising coal in a cupola, from the bottom of which the coke was withdrawn through a water seal. The true inception of the present era of vertical retorts may be said to have taken place in 1902, when Settle and Padfield, at Exeter, erected a semi-vertical retort in which the feed was continuous, but the coke was withdrawn only at intervals. This retort and its performance will be fully discussed elsewhere, as although it was afterwards a failure, it embodied some most valuable features.

This year also saw the inception of the vertical retort in Germany, which was also patented in England. In Bueb's patent, which is dated 7th July 1902, he sets forth the trouble in the early forms of vertical retort from the gas in the lower part of the charge having to traverse the column of incandescent coke above it, and proposes to overcome this by heating the retort only on three sides, and having a series of nostrils on the cool side through which the gas could escape from all parts of the charge. The fallacy of such an arrangement must soon have become manifest, as by July 1904 an experimental setting of verticals was at work at Mariendorff, the side exits having been abandoned, and the gas allowed to find its way through the carbonising coal, and this

retort was the subject of an English patent dated 19th January 1904.

In the meantime, on 27th July 1903, Messrs Woodall and Duckham took out their first patent, which embodies a principle far more important than any touched by the German experimentalist, that is, that, good as are the results obtained with the vertical retort working intermittently—*i.e.* by putting in a full charge of coal, carbonising and drawing, and then recharging, in the same way as with the old form of retorts—great improvements could be effected by making the process continuous—as was first attempted by Settle—so approaching more nearly to uniform conditions of carbonisation.

This patent shows the principle of making a continuous discharge of coke from the bottom of the retort govern an automatic coal feed at the top. In 1905 Young and Glover patented, on 17th November, a continuous vertical system based on the form of the shale retorts of which Young had made a life-long study. The main difference in this system from the Woodall-Duckham consists of the discharge of coke being independent of the coal feed, and that an empty space of constant dimensions is left above the coal, to form a cracking and fixing chamber for tar vapour.

In 1908 the water seal used to close the bottom of the Woodall-Duckham retorts was replaced by a better arrangement, and an ingenious coke remover was added to bring down the mass of carbonised material more regularly.

1909 saw the inception of the Glover-West system, John West of Manchester having brought his engineering knowledge to bear upon the constructional details of the Young and Glover retort of 1906. In this system there was introduced a cooling chamber for the coke, in which the heat from it was communicated to the secondary air supply, by passing the air through a jacket surrounding the coke cooler. The empty space at the top of the retort was done away with,

and the coke withdrawal was made to govern the coal feed.

Since then material improvements have been made in all the three existing systems of verticals, chiefly in details. The vertical retort is destined to play so important a part in the carbonisation of the future that the Dessau, Woodall-Duckham, and Glover-West installations must be dealt with at some length.

The principal installation of Dessau verticals in this country is at the Ayres Quay works of the Sunderland Gas Company, where under the able management of Mr C. Dru Drury, they have been working since 1909.

The installation consists of a bench of six beds of ten retorts each, the setting being in two rows of five. The dimensions of each retort are 13 feet $1\frac{1}{2}$ inches long, tapering from 9 inches by $22\frac{1}{2}$ inches at the top to $13\frac{3}{4}$ inches by $27\frac{1}{4}$ inches at the bottom. The installation is capable of carbonising $58\frac{1}{2}$ tons of coal per twenty-four hours, which, with deductions for scurfing, amounts to 400 tons per week, and yields, with steaming, 720,000 cubic feet of gas per diem, or, approximately, 12,630 cubic feet per ton of coal.

The arrangement and setting of the retorts is seen from the cross-section of bench, fig. 1.

Each retort takes a little under half a ton of coal and requires twelve hours for its carbonisation, including two hours of gentle steaming. To prevent any sticking or hanging up of the charge, the removal of carbon deposit from the inner face of the retort has to be carried out regularly, and to do this two retorts per day are left out of action, so that every retort is scurfed on the average once in five and a half weeks.

The setting is fired from a producer deep enough to hold an excess of coke, which ensures a good producer gas of constant composition, and the flue temperatures vary from 2390° F. to 1760° F. in the third chamber.

The pressures at the bottom of the retorts are high during

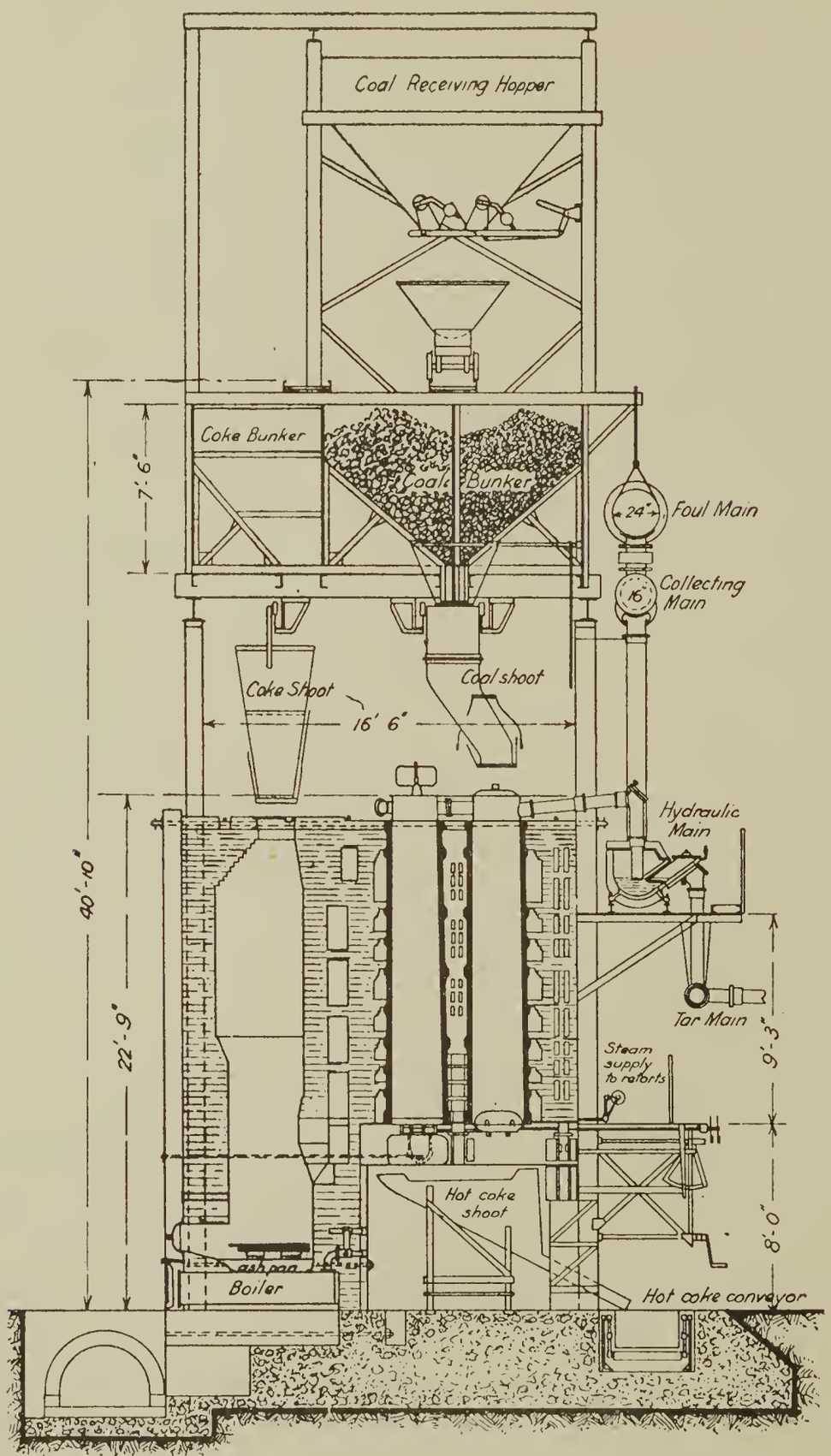


FIG. 1.—Dessau vertical retorts.

the first two hours, and then gradually fall until after the sixth hour they are negligible, whilst at the top they vary from level gauge to one-tenth.

The coke used as fuel is 13·96 per cent. of the weight of coal carbonised, and the gas produced 12,028 cubic feet of 17·55 candle gas from second-class Durham coal without steaming, but with steaming the fuel rises to 17·8 per cent. of the coal carbonised with an increase up to 13,000 cubic feet of gas, and consequent fall in illuminating power.

The process is intermittent, but, the retorts being emptied every twelve hours, the condition of the retort and the heats can be observed readily, whilst if any sticking or hanging of the charge takes place it is more easily dealt with than in a continuous process.

In the Woodall-Duckham continuous vertical retort system the principle is adopted of a continuous descent of the carbonising coal through the heated retort, time and temperature being so adjusted that the action is completed by the time the bottom of the retort is reached. The advantages of a continuous system of carbonisation are so self-evident that it has always been felt that ideal conditions could be approached only when a successful process for accomplishing it was perfected; but the difficulties to be overcome have been so great that until Settle and Padfield and Woodall and Duckham in 1902-3 started experimenting on these lines, it seemed almost impossible to achieve it; and in the ten years that have elapsed since the inception of the idea of applying the vertical retort to continuous gas manufacture, such advances have been made that continuous carbonisation is not only a practical success, but in another ten years will have established itself probably in all save the smallest works.

The Woodall-Duckham retorts are 25 feet long, gradually tapering from 4 ft. 3 ins. by 8 ins. wide at the top to 5 ft. 3 ins. by 20 ins. wide at the bottom, and they differ from other verticals in being built up of grooved and tongued bricks,

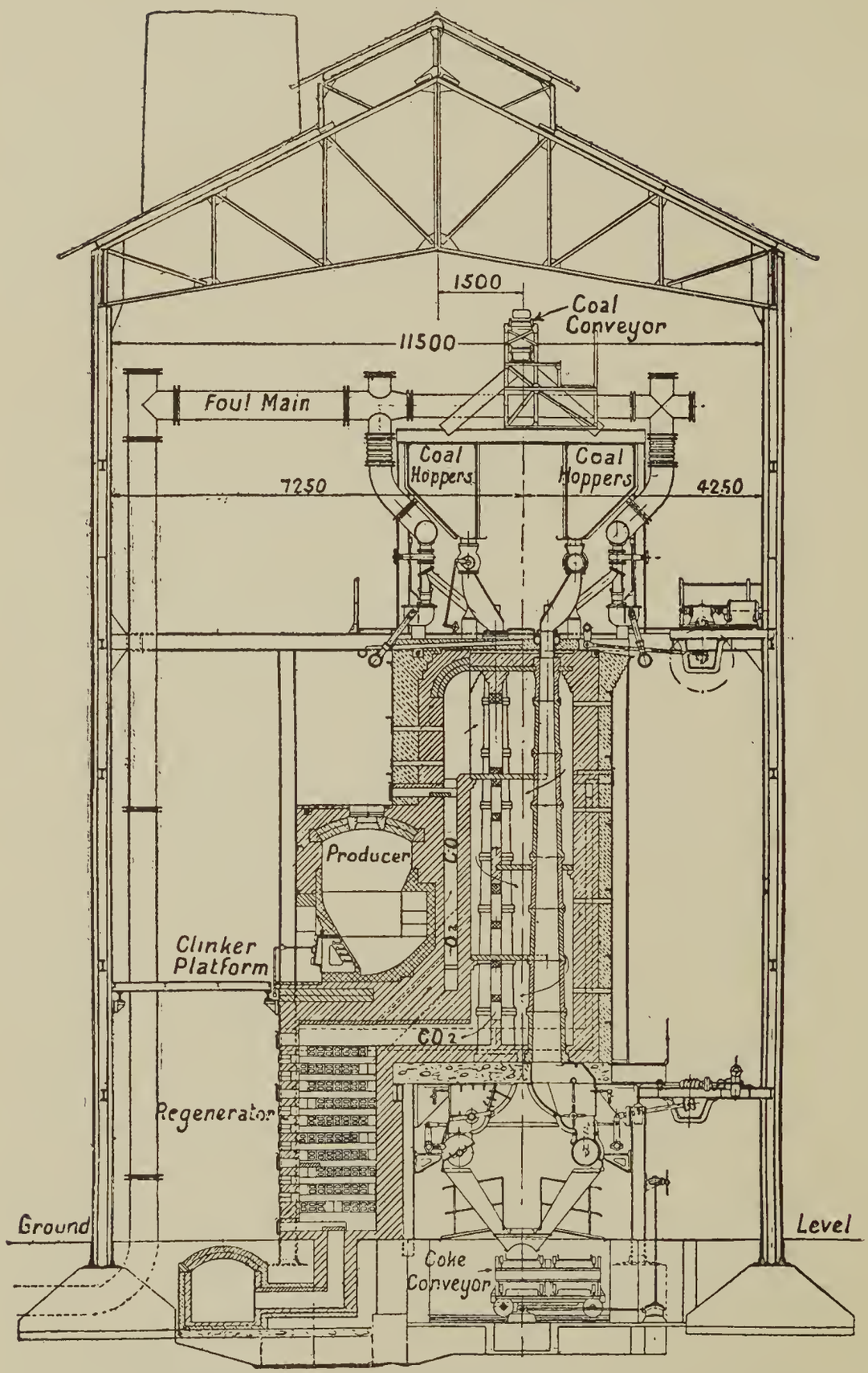


FIG. 2.—Woodall-Duckham vertical retorts, Lausanne plant.

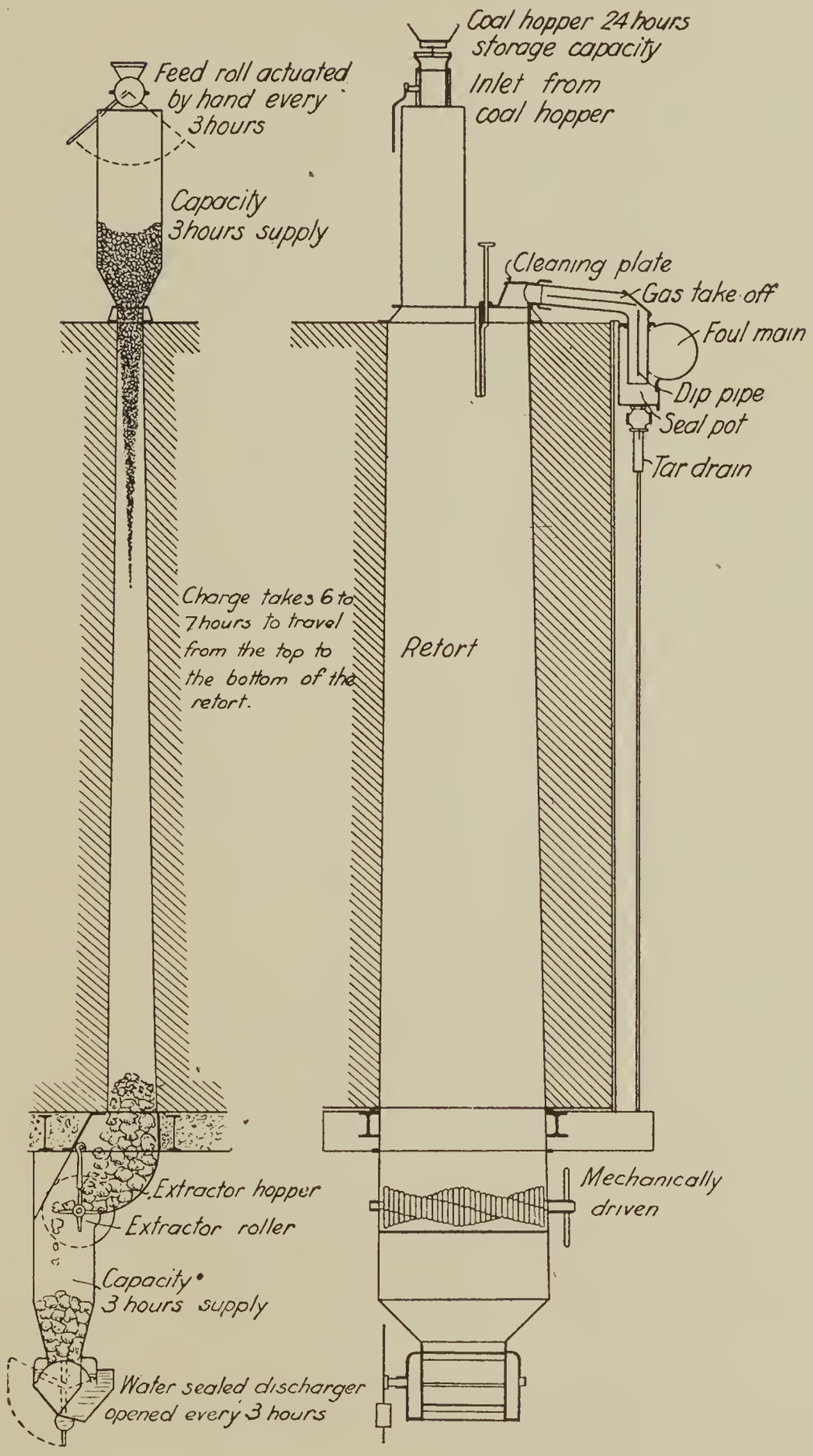

Coal hopper 24 hours storage capacity
Inlet from coal hopper
Feed roll actuated by hand every 3 hours
Capacity 3 hours supply
Cleaning plate
Gas take off
Foul main
Dip pipe
Seal pot
Tar drain
Charge takes 6 to 7 hours to travel from the top to the bottom of the retort.
Retort
Extractor hopper
Extractor roller
Capacity 3 hours supply
Water sealed discharger opened every 3 hours
Mechanically driven

FIG. 3.—Woodall-Duckham retort, showing charging and discharging arrangements.

panelled at the back, so that whilst leakage at the joints is reduced to a minimum, the transmission of heat to the charge is aided and the heating surface increased on the flue side. A good idea of the general features of the installation is given by a cross section of the Lausanne plant (fig. 2), from which it will be seen that the producer gas and secondary air from the regenerator meet at the top section of the retort and burn downwards, so as to produce the highest temperature where it is most wanted, *i.e.* at the spot where the cold coal is entering the carbonising area.

The arrangements for changing and discharging are shown in fig. 3. These are the parts of the installation that have given the greatest trouble to get right, as upon their smooth working depends the success of the installation, and they are, as at present fitted, the outcome of five years of experimental work.

In order to prevent the sudden fall of the coke in the retort on opening the bottom door, a cast-iron hopper or coke chamber is attached to the bottom of the retort, the back of the chamber being made of a curved iron plate on which the end of the coke column rests, and the coke is prevented from slipping down by the arms of an extractor roller shown in fig. 4.

The extractor consists of a series of cast-iron cross pieces mounted on a shaft, each cross piece being arranged slightly in advance of its neighbour, so as to form what are practically helical blades. As this slowly revolves the same amount of coke is withdrawn throughout the whole of the revolution and keeps the travel of the charge in the retort constant without breaking up the coke to an undue extent. Hanging weights are suspended from a shaft immediately above the extractor and prevent any passage of coke independent of its revolution.

The normal rate of movement of the extractor is one revolution per hour, but a screw adjustment enables this to

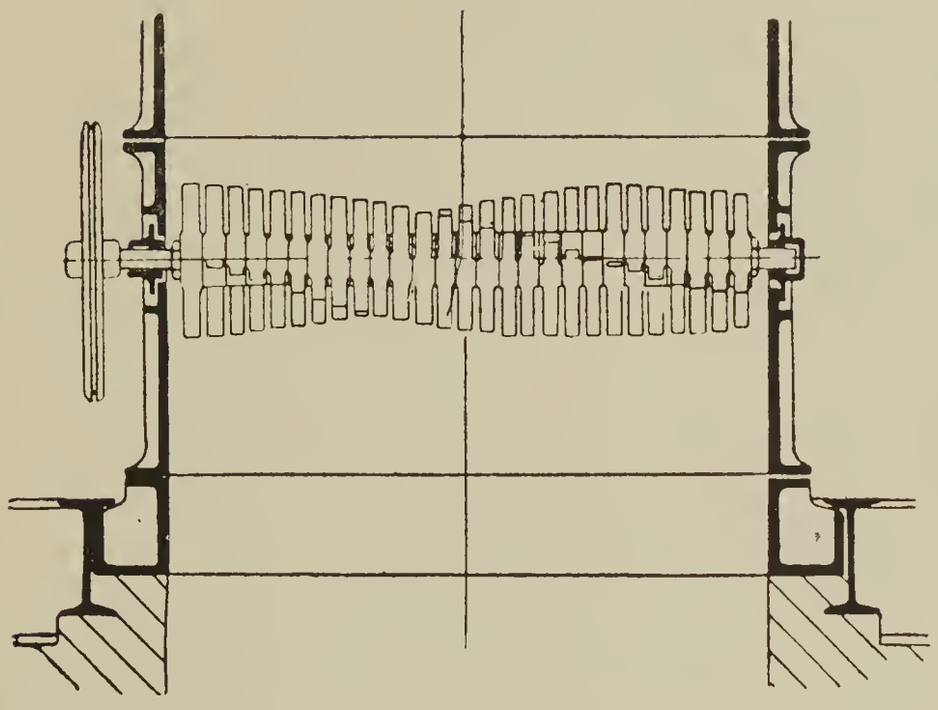


FIG. 4—Longitudinal section of extractor roller.

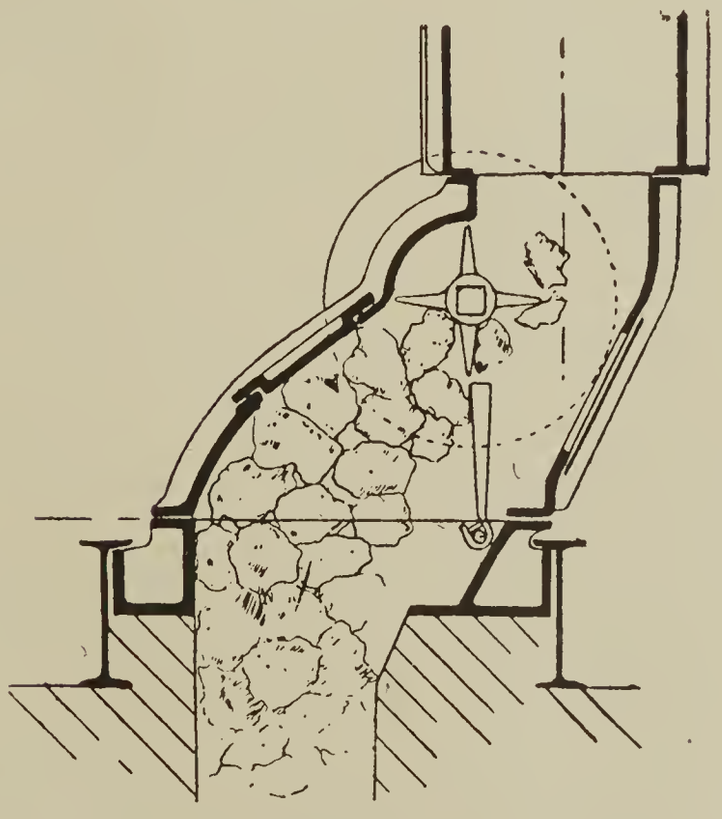


FIG. 4A.—Cross section of extractor roller.

be varied according to the character of the coal used. The period occupied from the entrance of the coal at the top of the retort to its discharge at the extractor is from seven to eight hours.

The extractor is driven by a wedge pawl working in a grooved wheel, and is driven by a rocking shaft extending the length of the bench (fig. 5). The coke, after passing

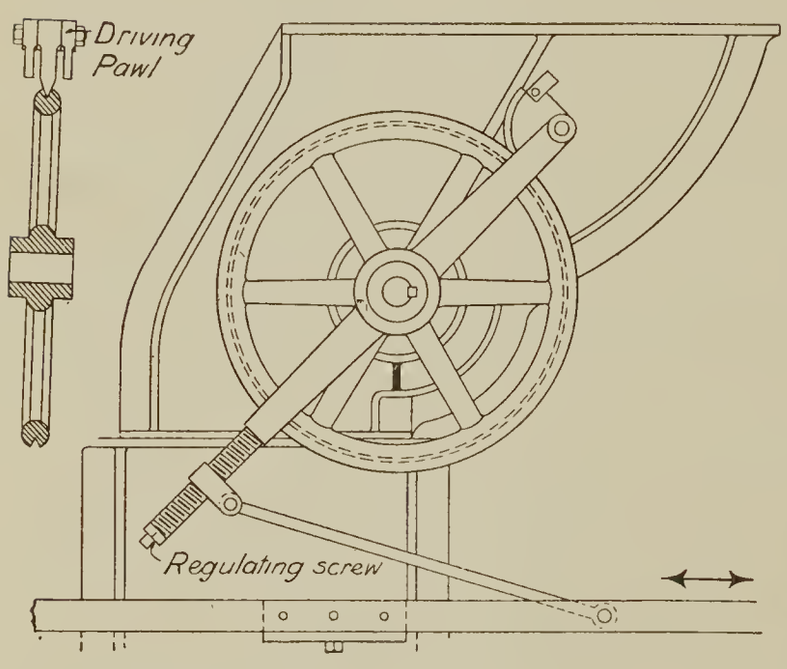


Fig. 5.—Extractor drive.

Fig. 6.—Coke discharge.

the extractor, falls into a cast-iron receiving hopper, which holds the coke from three completed revolutions of the extractor, or three hours' discharge.

Several devices have been tried for the discharge of the coke from the hopper, but the one fitted to the latest installations is a water-sealed door, shown in fig. 6.

The small amount of water present in the seal serves to keep the casting cool, but is never in contact with the coke, which, when necessary, is quenched by a small spray playing upon it in the storage hopper; but the coke leaves the

apparatus practically in a dry state, and at a temperature of about 140° F.

It is evident that it is the rate of travel of the extractor which governs the rate of passage of the charge through the heated zone ; and the feed at the top of the retort is so arranged that the supply of fine coal simply follows the sinking column of coke and keeps the retort full, with the exception of a small space leading to the gas exit, which is partitioned off and can be regulated in size by a sliding plate.

In order to permit of these arrangements, the top of the built-up retort is closed by a cast-iron mouthpiece, to which is fixed the coal feed, gas take-off and regulating division plate, as shown in figs. 7 and 8.

The coal feed consists of a gas-tight hopper made of mild steel, and so arranged to one side of the retort that it leaves free access to the interior of the retort should need arise, as in the case of a charge hanging up and not passing down regularly to the extractor. This hopper is closed at the top by a gas-tight valve, on opening which coal is fed in from a store hopper above, the operation taking only a fraction of a minute,

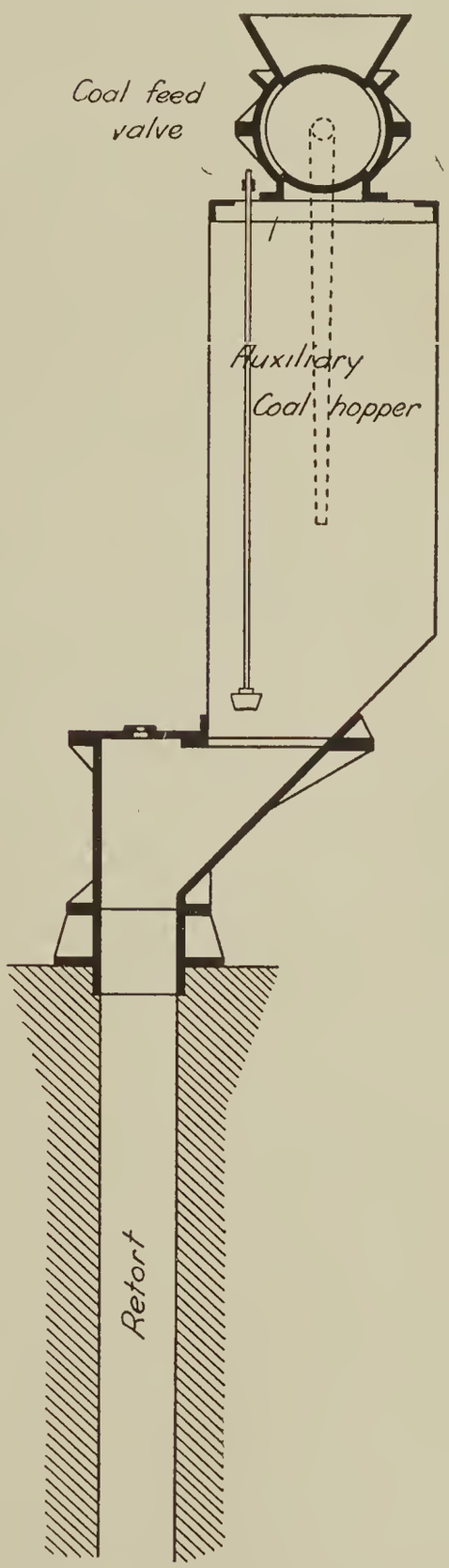


FIG. 7.—Cross section of top of retort.

and is necessary only once in three hours, the hopper being so proportioned as to contain enough coal to supply the coke extracted by the three revolutions of the extractor at the bottom.

It is clear that in order to obtain continuity in the process a certain amount of complexity in the working arrangements becomes a necessity, and in comparison with the crude simplicity of the older methods awakens mistrust in the gas manager's mind, whilst, naturally, the supporters of the

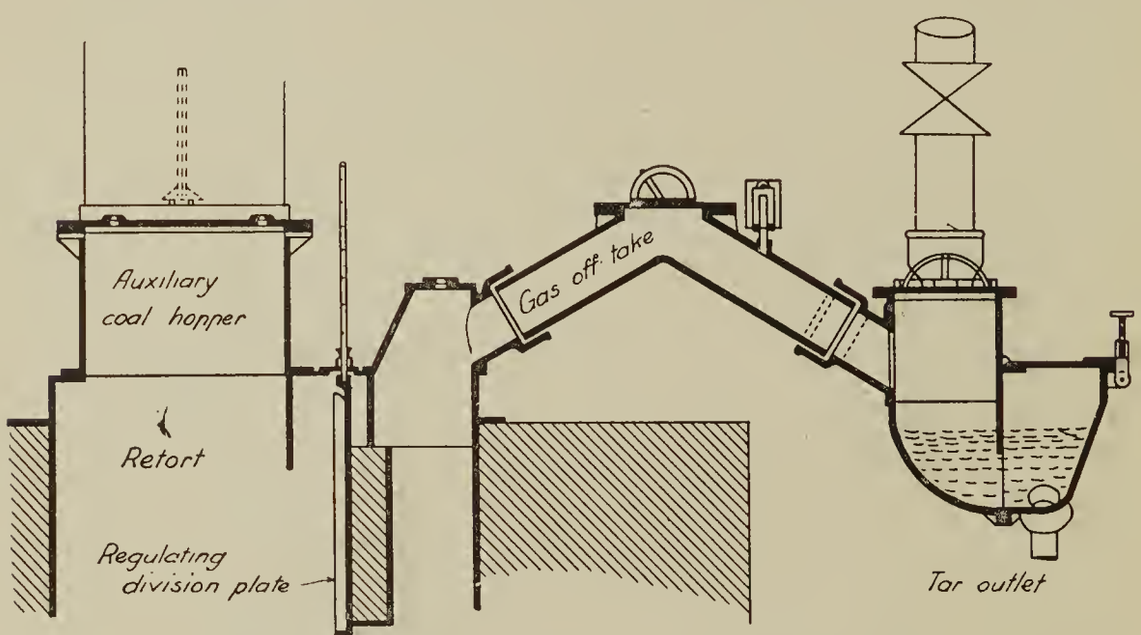


Fig. 8.—Longitudinal section of top of retort.

intermittent systems in vertical carbonisation make as much as possible of the fact that they can freely inspect the interior of their retorts every twelve hours, and keep them scurfed and free from obstructions likely to hang up the charge.

Extended experience, however, will show that there is very little in this contention. The formation of the carbon deposit or scurf in a vertical retort working continuously is a sign of faulty management, as all the hydrocarbons capable of being broken up, with deposition of carbon, should be out of the carbonising mass before the charge has travelled half-way down the retort, or at any rate remain only in the

core, in escaping from which they would deposit their carbon in the coke and not on the retort, so that any hanging up from this cause should be only near the top of the retort, and is easily freed by a thrust from the clearing rod through the sight hole at the top. Formation of the scurf in the lower part of the continuous vertical means that green coal has got too far down, and that there is something radically wrong with the working of heats, feed, or removal. Mechanical hanging up, due to straining, bulging, or ledges in the retort, may take place in any part, and means shutting down and proper adjustment, or endless troubles will arise.

The Woodall-Duckham system is at work not only in several English works, but also in America, and at Lausanne in Switzerland, and the general run of results with various coals is 12,900 cubic feet per ton, whilst the fuel account is very low, being only a little over 12 per cent.

The second continuous vertical carbonisation process is the Glover-West, which is founded upon the Glover-Young system patented in 1905, and more or less based on the Scotch shale retorts, which for more than half a century have been used for the distillation of shale oil.

The original Glover-Young installation has now been abandoned, and is sufficiently explained by the section (fig. 9).

Its marked differences from the Woodall-Duckham system were in leaving an empty space at the top of the retort, passing the escaping gases and vapours through the coal hopper, and, as a necessity, making the discharge and feed more or less independent of each other.

In the Glover-West system, however, these features all disappeared, and a very distinct improvement was made in leading the secondary air for combustion in the flues through a chamber jacketing the cooling hopper for the coke, so that instead of quenching the coke by a fine spray, the coke yields its heat to the in-going air, and by this regeneration reduces

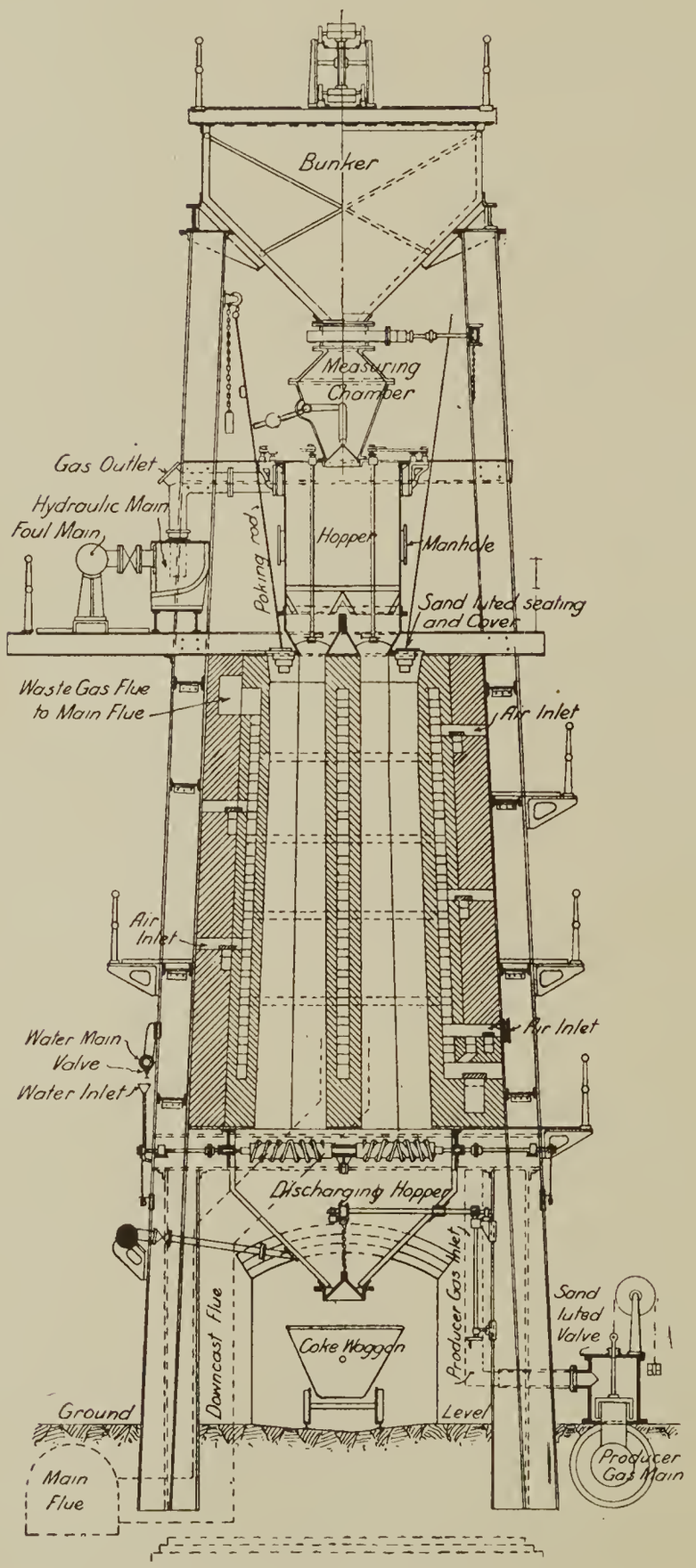


FIG. 9.—Glover-Young retort.

further the fuel consumption, which is given by Mr J. G. Newbigging as 10·04 per cent.

An excellent paper on the system was read by Mr

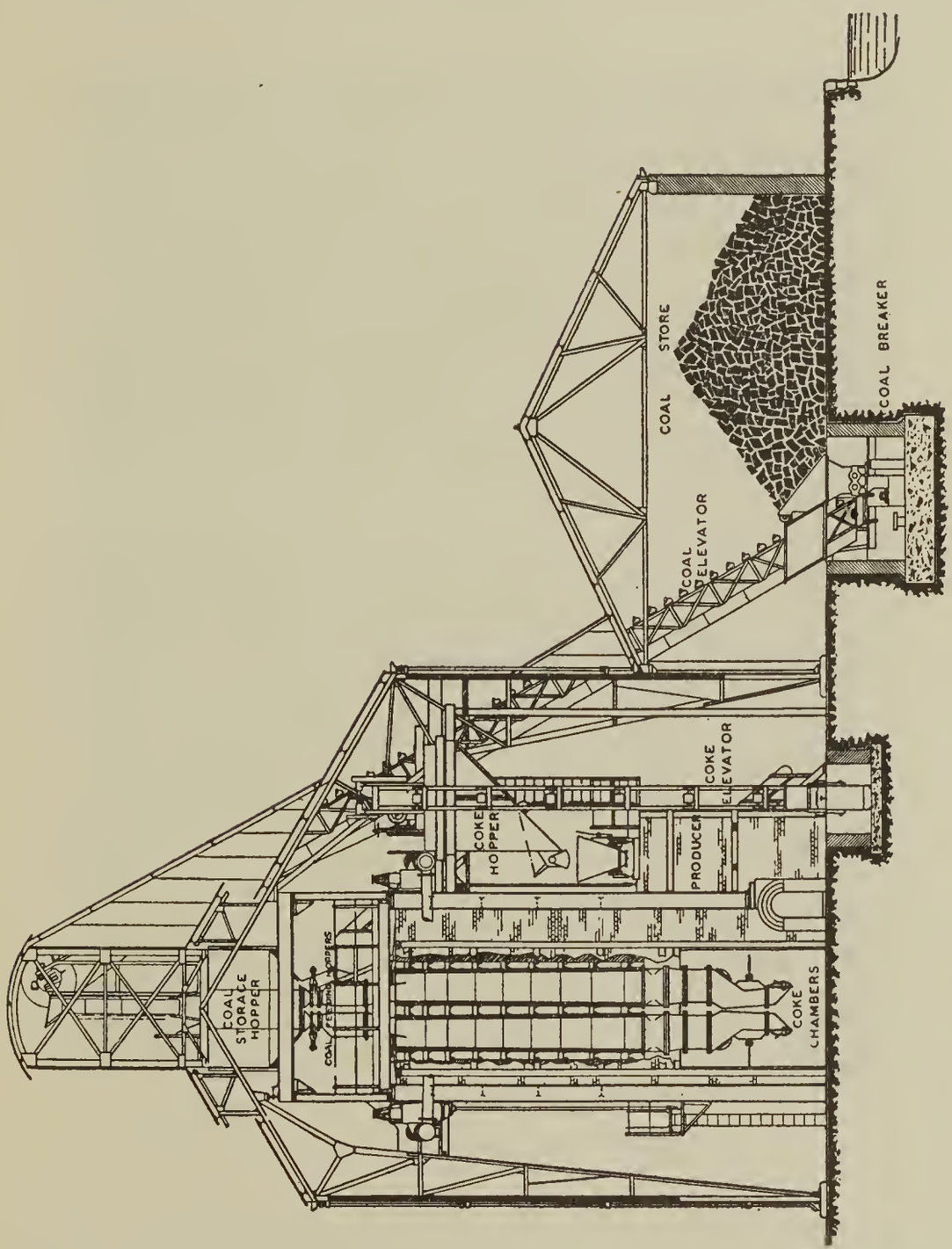


Fig. 10.—Sectional elevation of Glover-West vertical retort house and coal store.

Newbigging at the 1911 meeting of the Institution of Gas Engineers, from which it may be gathered that the working at the Droylsden branch of the Manchester gasworks is

giving great satisfaction, and upholding the results previously attained at St Helens.

The Droylsden installation consists of two settings of eight retorts, the nominal capacity of the plant being 500,000 cubic

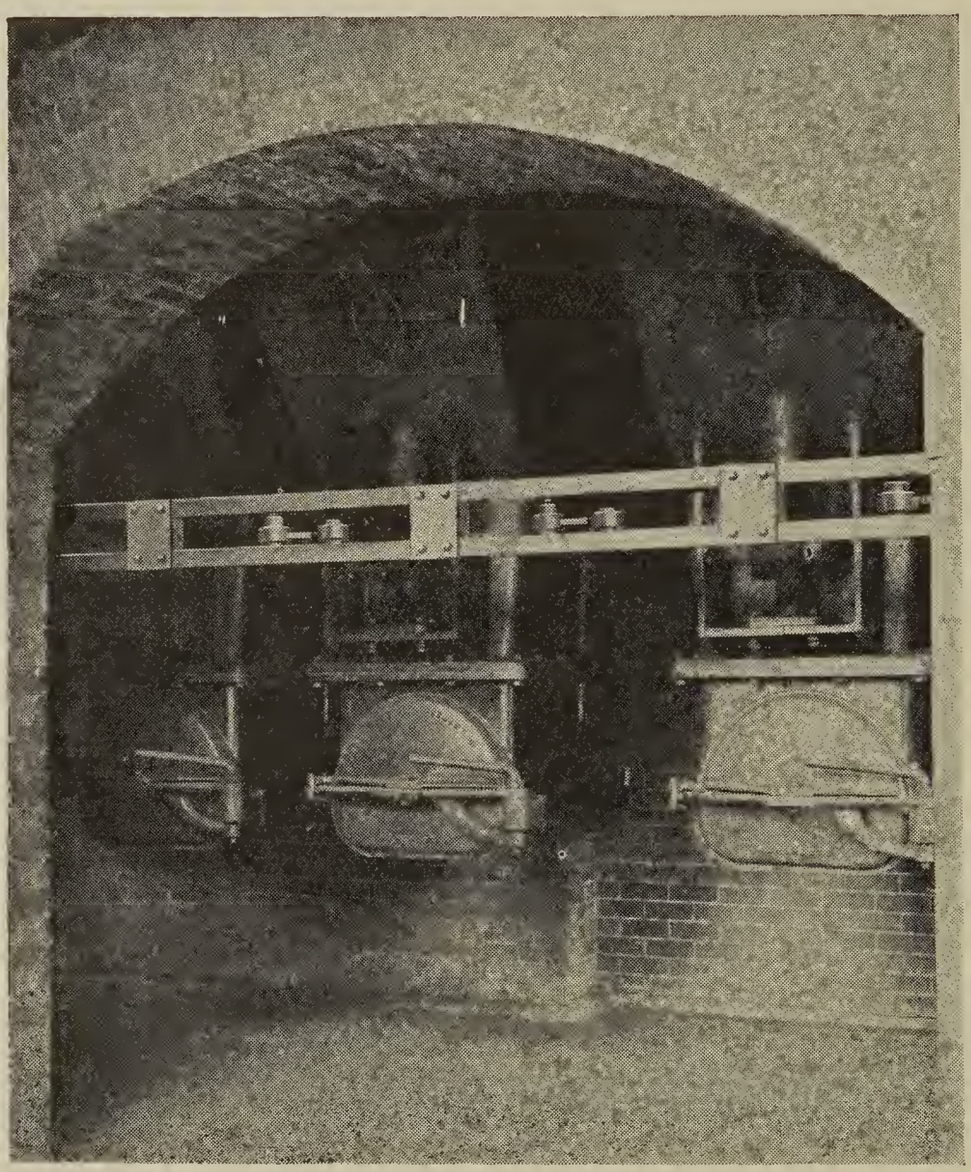


Fig. 11.—Glover-West coke chambers: Front view.

feet of gas per twenty-four hours, an output, however, which has been exceeded several times. Each setting of eight is subdivided into two sections of four retorts, this arrangement being of use in the event either of the total output not being required, or of any one section needing to be shut down.

Each setting is provided with its own producer, from which gas ascends to the combustion chamber, each half of the setting having its own flue. The general arrangement of the retorts in the setting can be seen from fig. 10.

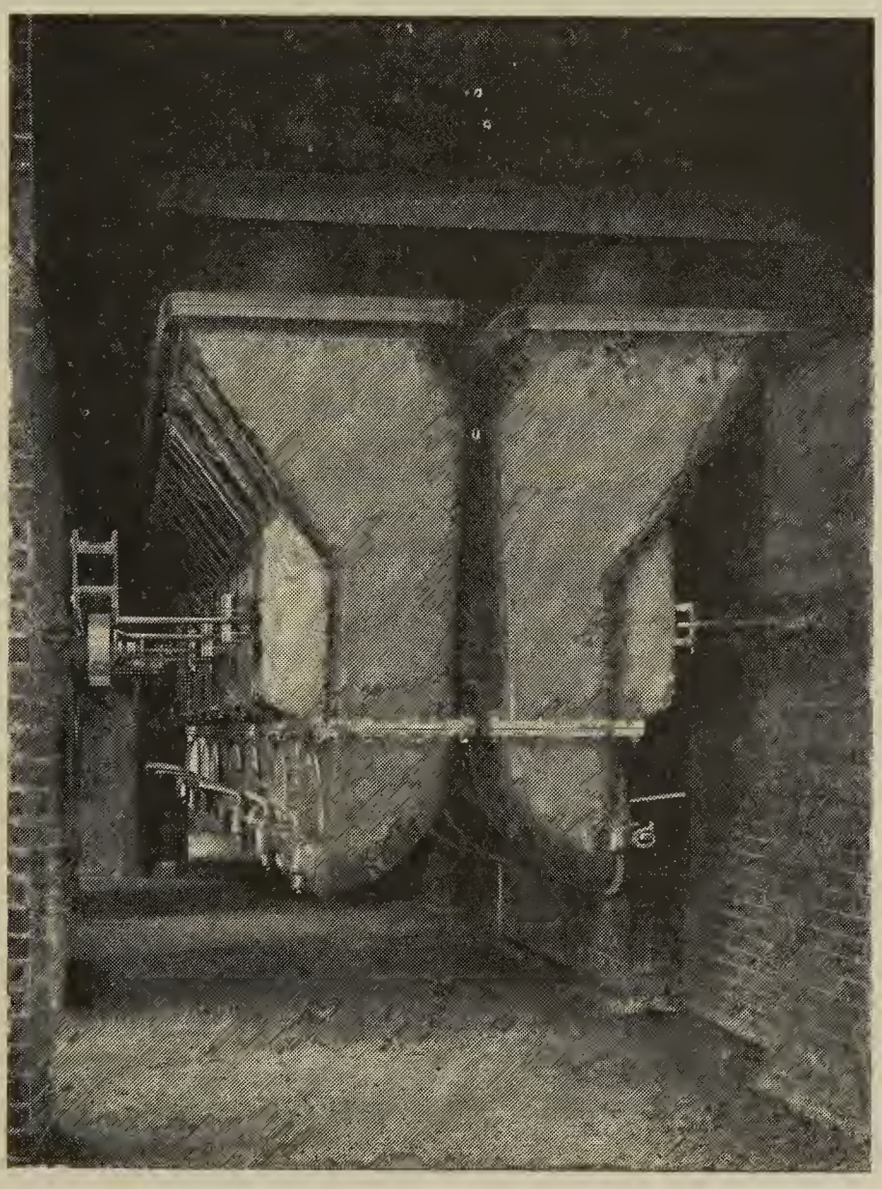


FIG. 12.—Glover-West coke chambers: Side view.

The retorts are oval in section, tapering from 30 by 10 inches at the top down to 36 by 22 inches at the bottom. The total length is 20 feet. One of the special features of the setting consists in there being a cast-iron chamber 3 feet deep at the bottom of the retorts, which forms a cooling

chamber for the coke, and enables the heat given off by it to be imparted to the air for the secondary combustion. Below this coke cooling chamber each retort is fitted with an extractor, which consists of a slowly revolving vertical screw made in halves, so that by undoing a catch and partially revolving one half a space inspection and access to the retort is afforded.

The power for driving all the extractor screws is obtained from a small gas-engine, the power being transmitted to the coke extractors by a belt drive with a speed reduction device and reciprocating side rods, from which levers and ratchet pawls with ratchet wheels drive the coke extractors.

The extractor discharges the coke into the bottom hopper, which has a self-sealing lid. An idea of the bottom hopper or coke chamber can be gathered from figs. 11 and 12. From this hopper it is removed at intervals of two hours. The arrangements at the top of the retort are almost identical with those of the Woodall-Duckham plant. The gas passes off from each retort at the side of the base of the coal-feeding hopper, a partition being provided to keep the space free from the coal, which descends on the other side of the partition from the sealed hopper.

All the experience which has been gained with this class of retort points to wear and tear being small. The St Helens installation, although it has been working for something like three years, is still in excellent condition. With this system, as with the Woodall-Duckham, the enormous advantage that at first strikes any one accustomed to the old processes of carbonisation is the smooth and noiseless working of the plant, with absolute freedom from smoke and steam, the coke being fed out at the bottom, cooled down and dried. It must be remembered that throughout the whole process in continuous carbonisation the retorts are yielding gas of perfectly uniform composition, which is in itself an enormous advance over the old bench of retorts, in which the newly-

charged ones were giving an 18-candle gas, whilst those in their fifth hour were giving a non-luminous product, the only guarantee of uniform quality in the holder being that the products of many retorts were mingling and mixing from the entrance to the hydraulic main to their exit from the purifiers.

The economies to be derived from carbonisation in bulk have, on the Continent, led to still further advances in the size of the charge, and little more than four years ago chamber carbonisation was introduced at Munich, in which charges of three to eight tons of coal can be dealt with at a time. This method also has met with a large amount of success, a number of installations having been erected on the principles laid down by Ries, Koppers, and others.

This class of carbonising plant is intermediate between the ordinary intermittent gasworks practice and coke oven recovery plant, differing indeed from the latter only in the treatment of the gaseous products, and in some of the chamber processes adopting the principle of the inclined and vertical retort, in order to secure as much aid as possible from gravity in discharging the coke formed.

The history of the chamber setting as apart from coke oven practice may be said to date from 1901, when Ries and Schilling, at the Munich works, adapted an old setting for inclined retorts by building into it three chambers, taking a charge of one ton each, the floors of the chambers being set at an angle of 35°. The chambers were afterwards enlarged, and finally an installation of fifteen chambers in five settings was erected, and started work in the autumn of 1906.

The general arrangement of this installation is shown in fig. 13. Each carbonising chamber takes a charge of two and a half to three tons, and the time taken to carbonise it is twenty-four hours. This system was reported on by Dr Bunte in 1907, who found that an average of 11,342 cubic feet per ton of Saar coal could be obtained of a gross calorific value of 626 B.Th.U. per cubic foot.

Dr J. Bueb criticised these results, and pointed out that if a Saar coal took twenty-four hours to carbonise, a Durham coal would probably take thirty-six, so that one of the claims to economy, *i.e.*, being able to do away with night shifts,

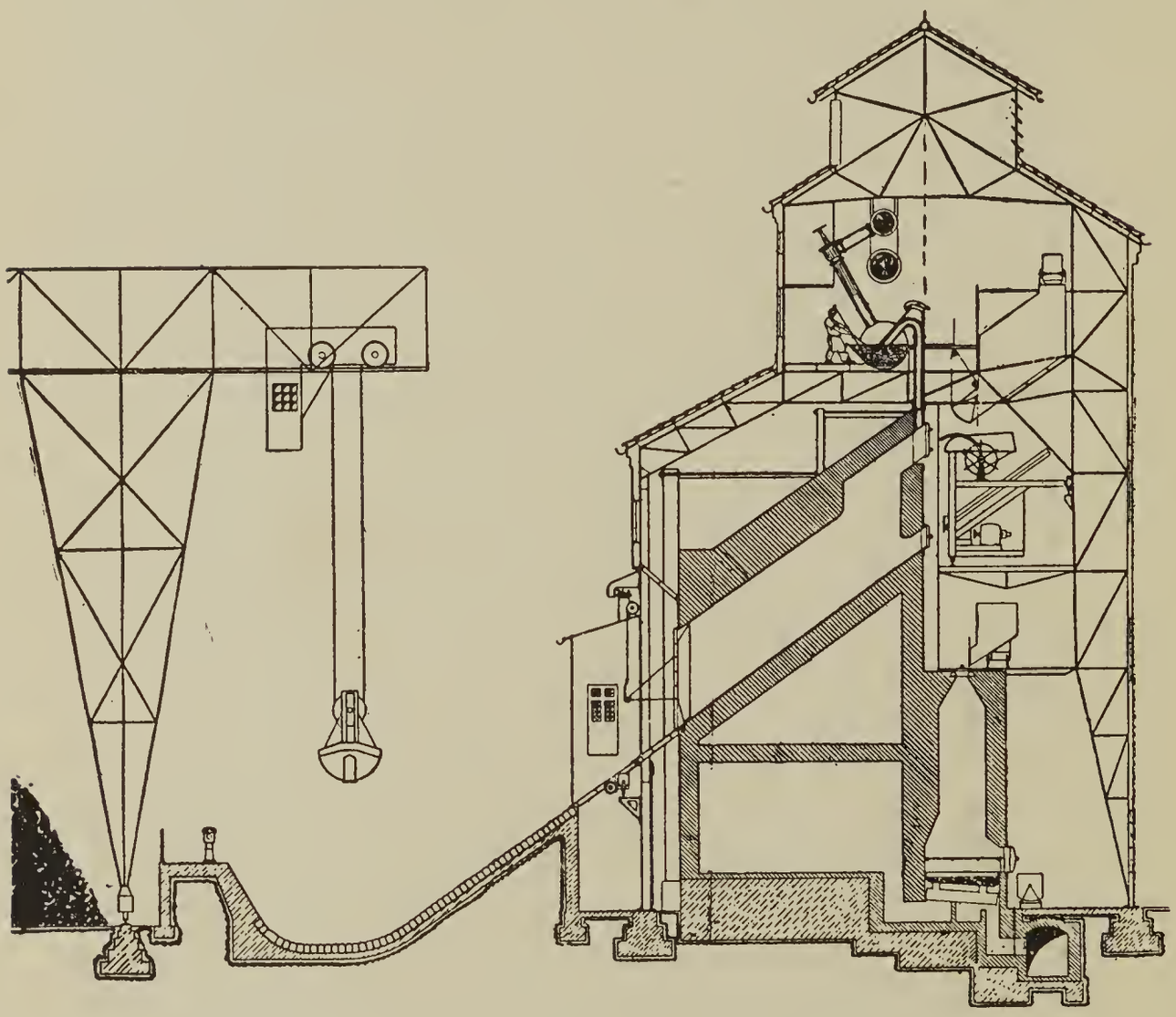


Fig. 13.—Cross section of the Munich carbonising chamber.

was a fallacy; but even if this were so, the economies in handling are very great.

As Dr Lessing has pointed out, the history of chamber carbonisation affords almost the only exception that can be brought forward of the gas industry accepting a new process with little or no experience to support it. The principle has spread with great rapidity on the Continent, although the

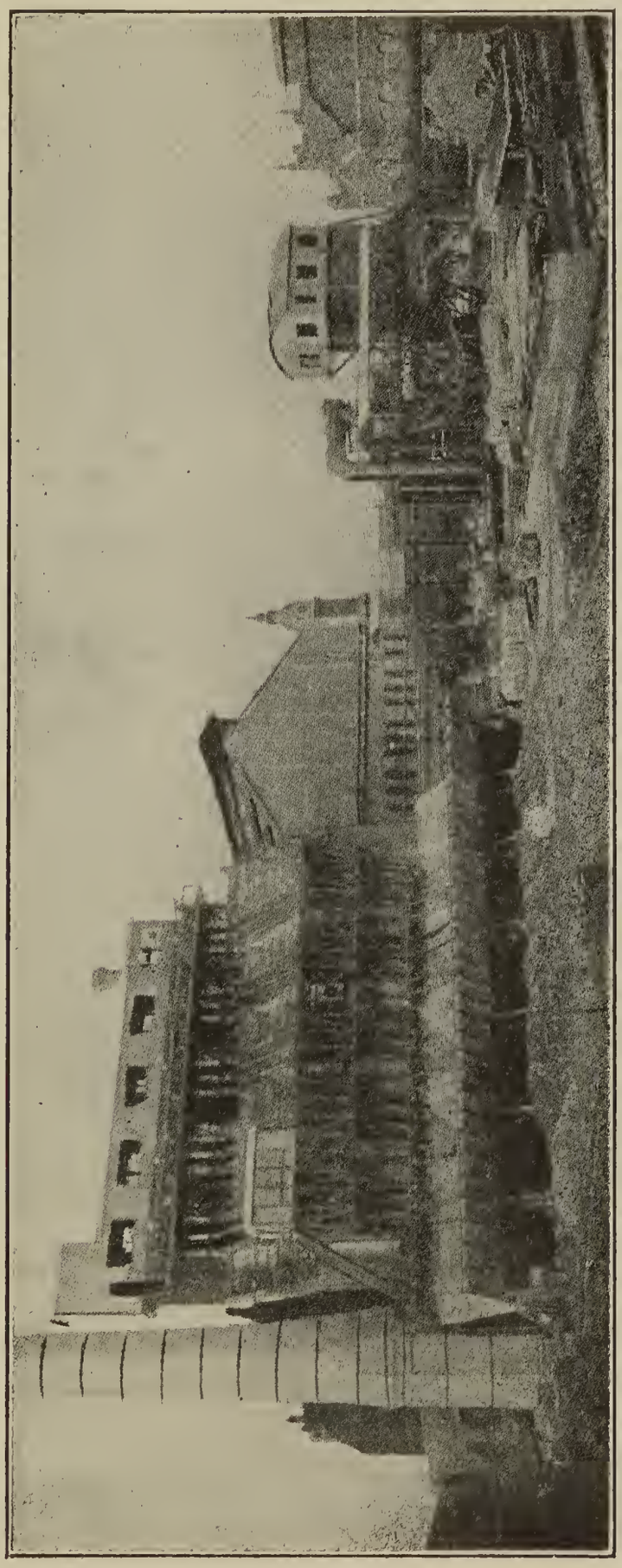


FIG. 14.—Battery of fifteen Koppers' chambers erected at the Vienna gasworks, with the gas-purifying plant on the right.

English gas manager has not, so far, been tempted to try it.

No sooner was the Munich installation successfully working than a battery of chambers of nearly double the capacity

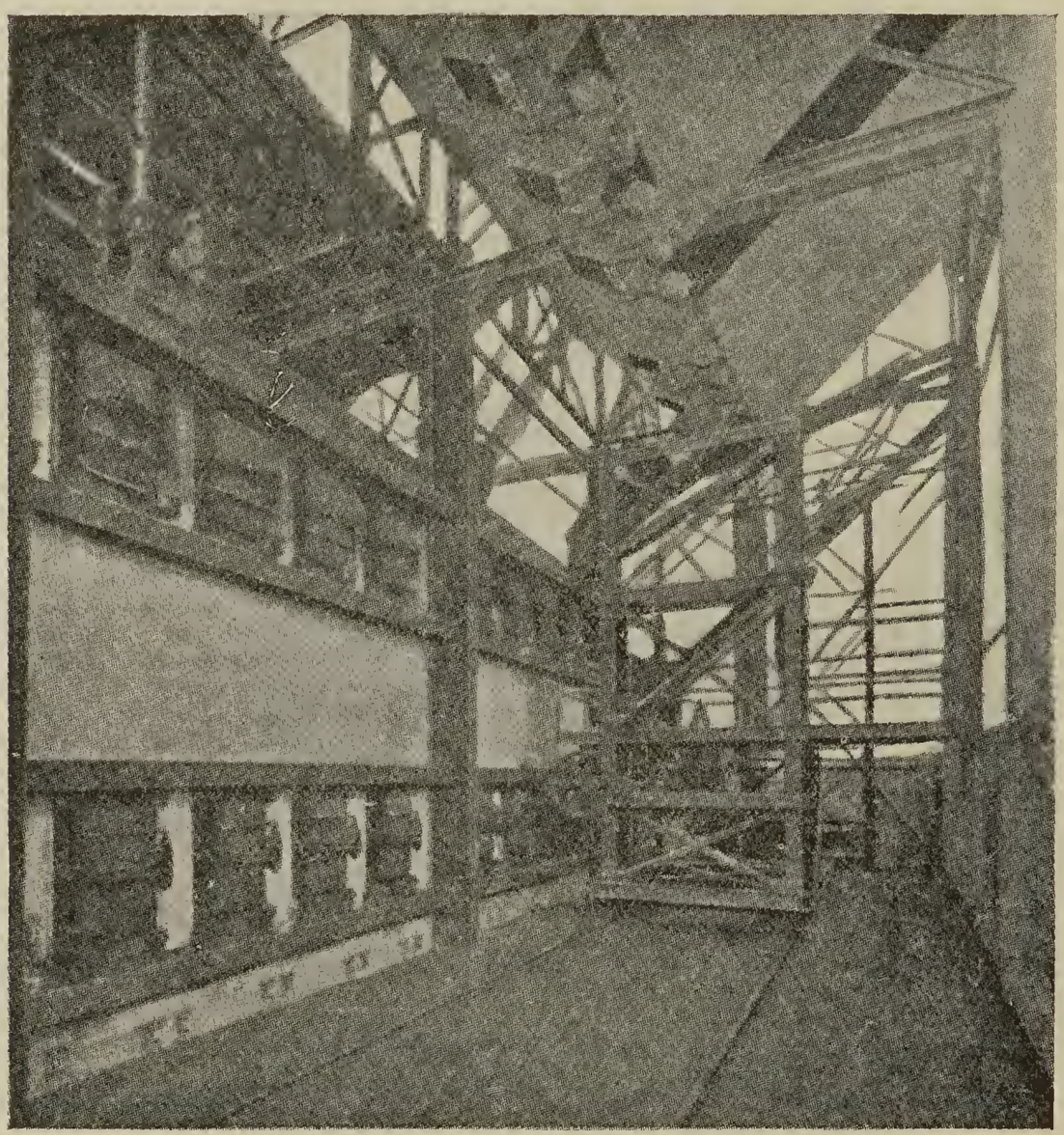


Fig. 15.—Klönne's inclined chamber ovens at Königsberg: Charging side.

was erected at Hamburg. It consisted of ten settings of three chambers each, inclined at an angle of 35°. The chambers are 24·6 feet long by 7·4 feet high, the two outside chambers being 1 foot 8 inches wide, and the middle chamber 2 feet. The carbonising period is twenty-

four hours, and the capacity of the three chambers 17·5 tons.

In a third installation, at Moosach, the size was still

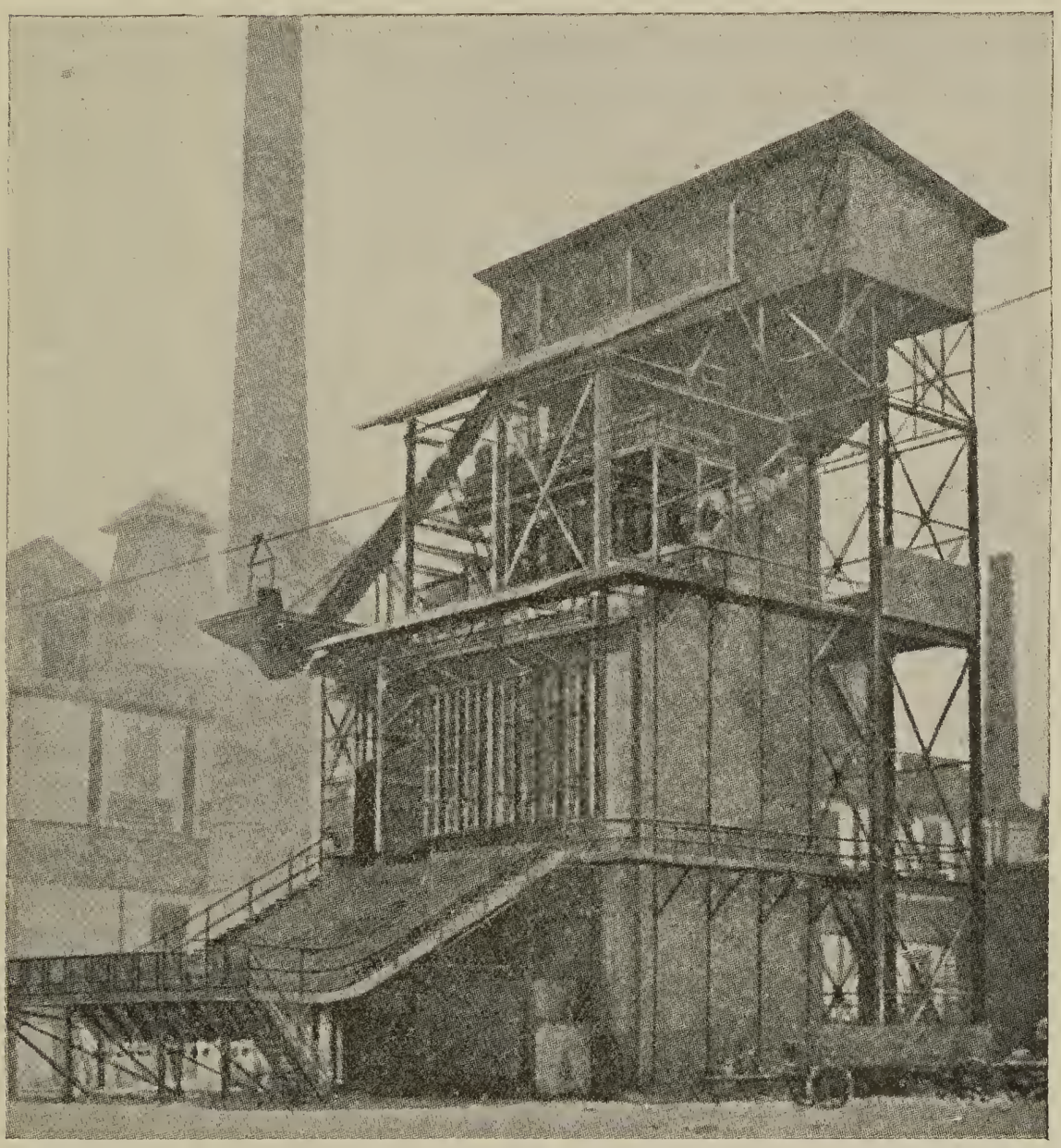


Fig. 15a.—Klönne's inclined chamber ovens at Königsberg: Discharging side.

further increased, the chambers being made 28·7 feet long, the height and width being the same as before, and the installation consisted of twelve settings of three chambers each. At Bochum, an installation, also on the inclined system, was

designed and erected by Koppers, and started work in 1908, whilst a still larger battery of fifteen chambers was erected at Vienna (fig. 14).

At Rotterdam, horizontal chambers were introduced in the same year, on the Klönne principle, and inclined chambers by the same firm at Königsberg.

Messrs Knoch have also erected inclined chambers at several towns, whilst Klönne at Dortmund and Horn at Hecklingen have introduced vertical chamber ovens.

All these types have had their supporters, and on the Continent something like 1000 chambers on various systems have been erected, but nearly all the older systems have undergone modification, and there is a noticeable tendency to revert to the horizontal chamber with mechanical coke pusher.

The whole of this extraordinary development in chamber carbonisation has been due to economy in handling. It has been claimed that in some cases a labour charge of 9d. per 10,000 cubic feet has been reduced to $\frac{3}{4}$d.; but although this is an important item the initial cost of such a plant is very high, and the candle-power of the gas is below the English standard, although of a satisfactory calorific value. This fact has saved the English gas manager from having a fresh series of claims to consider; and by the time the illuminating standard has been consigned, together with its friend the flat-flame burner, to an unhonoured grave, and a calorific standard has taken its place, the continuous vertical system will have shown that the true path for the carboniser to follow is uniformity in treatment and rapid heating, rather than a twenty-four hours' stewing, if gas and domestic coke are his aim; whilst, if metallurgical coke is the desired result, the chamber will have some trouble to prove its superiority over some of the more modern forms of coke oven.

Many observers felt that the old horizontal retort could be made to yield better results than had hitherto been obtained, and Mr Charles Carpenter, at the South Metro-

politan Gas Company's works, found that great advantages may be obtained by packing the horizontal retorts full of coal (instead of only partly filling them) as had been suggested by Kunath in 1885, this doing away with the large space that had always been left above the charge of carbonising coal, and so eliminating to a great extent the baking of the gases and contact with the heated crown of the retort, thus giving

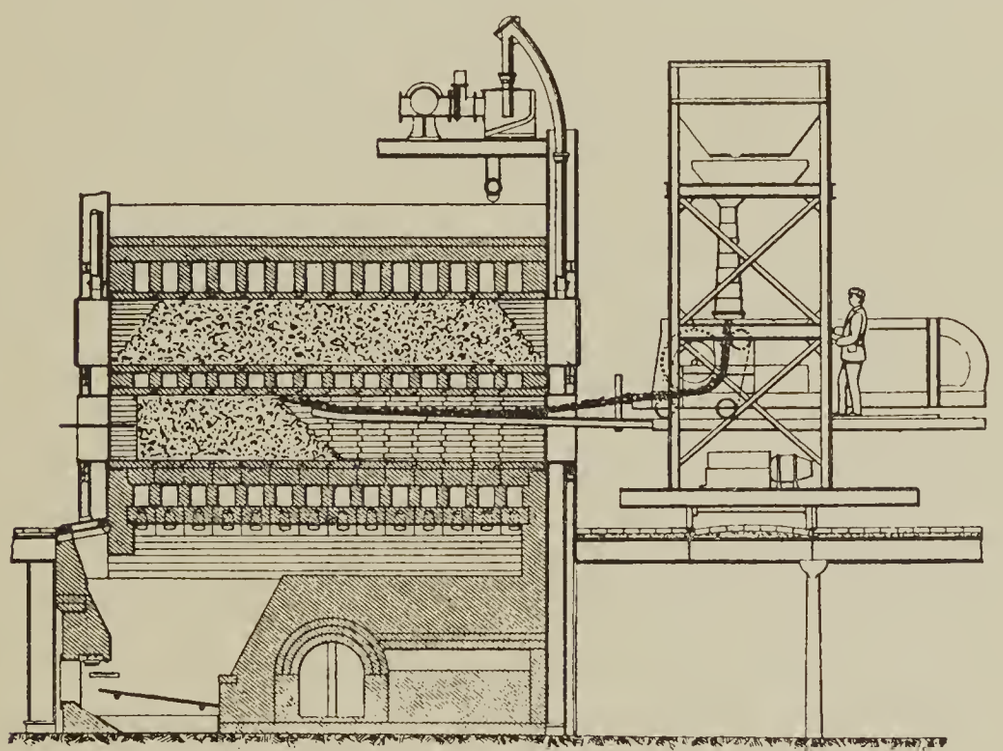


Fig. 16.—Chamber retort setting at Norwich.

a distinct advance in make and quality not only in the gas but in the tar.

In following the history of the rise of the gas industry one cannot help feeling that the part played by the introduction of mechanical stoking and discharge has hardly received the full mead of credit that it deserves. Without it the fully charged horizontal would have been an impossibility, and although in the course of time our friend of a century is bound to bow its head before the advance of the continuous vertical—in the same way that the mantle has swept away the flat-flame—yet the horizontal retort is making

a splendid effort to retain its pride of place, and the full charge will keep it alive for many years to come.

At Norwich, Mr Thomas Glover installed a form of retort which is a compromise between chamber carbonisation and a full charge in the horizontal (fig. 16). These so-called chambers consisted of oblong retorts 3 feet high, 1 foot wide, and 21 feet long, taking 21 cwt. at a charge, and carbonising it in twelve hours. The results obtained from them were excellent, but on further experience it was found that the fully charged horizontals gave practically the same result, and the use of the semi-chamber has been abandoned, or at any rate not extended.

If we attempt to differentiate between the modern methods of carbonisation, taking as a basis the gas yield per ton from a good gas coal, we find that there is but little to choose between them, the well-filled horizontals holding their own with the intermittent and continuous vertical retort systems, but as soon as we begin to consider other points, the continuous vertical retort begins to assert its superiority.

When we take the four leading systems and try to differentiate between them by the important item of fuel consumption, we find the best practice gives per 100 lbs. of coals carbonised :—

Horizontal.	Intermittent verticals.	Continuous Carbonisation.	
		Woodall-Duckham.	Glover-West.
14	15	12·1	10·3

So that here, as one would expect, the withdrawal of heat from the coke and utilising it to heat the secondary air gives the Glover-West process an advantage.

If we now take cleanliness of working, amount of nuisance to the neighbourhood of the gasworks, and uniformity in composition of the gas during the period of carbonisation, the continuous vertical retort stands alone. It is an impossibility to shoot or feed a heavy charge of raw coal into

a red-hot retort without getting an outrush of steam and smoke that permeates the atmosphere for a considerable distance, and means not only loss but stench ; whilst continuous vertical carbonisation also gives the further advantage that the coke, being cooled in the bottom chamber of the retort, needs little or no spraying when drawn, and steam is thus avoided.

The coke, tar, and sulphate of ammonia in all the new methods of procedure are an improvement upon the products from the lightly charged horizontal, so that not only from the scientific but also from the practical point of view the continuous vertical retort processes are the ones that show the real advance, and what is still more important is that they are the ones which offer a promise of improvement.

There are other points, however, which the gas manager must take into consideration in choosing a process, and these are : the cost of an installation, the cost of labour, and the ground space that the installation will occupy. At present the cost of the vertical retort installation, be it intermittent or continuous, is in most cases just about double that of the horizontal ; but, on the other hand, it must be credited with saving in labour and space ; nor should it be overlooked that the horizontal retort has had a century of experience lavished upon it, whilst the vertical is in its infancy.

I think enough has been said to show that we are well ahead of Continental practice, and if any one asked my advice as to their present carbonising methods, it would be to use full charges in horizontals until a scrapping of the plant becomes a necessity, and then to instal a continuous vertical retort system.

CHAPTER IV

COKE OVENS AND THEIR DEVELOPMENT

The early history of coke manufacture—Meiler coke—Beehive ovens—Modern improvements—American practice—Jameson's oven—Classification of coke ovens—The Coppée oven—The Appolt oven—Simon-Carvès recovery plant oven—The Otto recovery plant oven—Difficulties of heating the chambers—Illuminating gas from recovery coke ovens in America—Results—Differences between American and Continental gas chamber processes.

An old German carboniser named Stauf seems to occupy the same position with regard to oven coking that Murdoch does to the gas industry. Goethe, in describing a holiday in the Saarbruck district, tells of a visit he paid in 1771 to the old philosopher, whom he found living in a small hut on a hillside, endeavouring to cleanse coal from sulphur in a connected row of furnaces, with the object of using the coke for iron-smelting.

This attempt arose from the necessity of finding a substitute for charcoal, which up to that time had been the fuel employed for the recovery of iron from its ores, but which, owing to the depletion of the forests, was becoming so costly as to render its use prohibitive. When the idea of coking coal first arose, as might be expected, the same methods as in charcoal burning were employed, heaps of coal being ignited on the ground and the combustion checked by coating with damp coal dust. A small advance was soon made by building a brick shaft or chimney with openings in the side, to allow the passage into the shaft of the gases and volatile vapours issuing from the heap of coal piled around it, and so

arranged that the largest coal was nearest the middle. The mass was ignited by burning coal introduced into the shaft, and air inlets were made along the ground into the heap, the combustion being checked afterwards by coal dust, ashes, etc., spread over the outside. Such a method of carbonising was most wasteful, but it produced a good coke where a certain quantity of volatile matter was not a drawback; and "meiler coke," as it was called, is still made on a small scale.

In these processes the heat was given partly by the combustion of some of the coal, and partly by the gases and

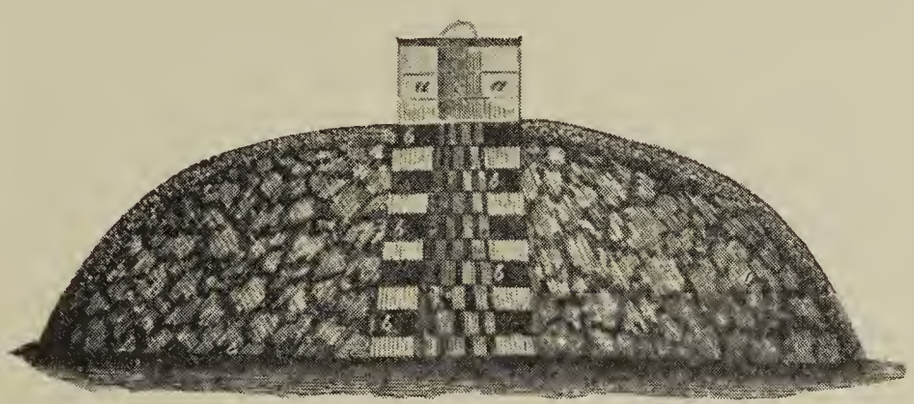


Fig. 17.—Coke meiler.

vapours, and the meiler heaps soon began to be displaced by "oven" coking, which gave a more uniform product and a larger yield of coke.

The early ovens were heated entirely by the combustion of the vapours and gases, together with a small proportion of the coal within the oven, no external heat being employed. These ovens, called "beehive ovens," on account of their domed tops, were 12 feet wide by 10 feet deep, and held a charge 10 feet in depth. The walls were 2 feet thick, and the ovens were built in groups to retain heat and minimise brickwork. They had a hole in the top of the dome $2\frac{1}{2}$ feet in diameter, which could be closed by a plate, and an opening in front for charging or drawing, fitted with a sliding door in an iron frame, the door being provided generally with air

inlets adjustable at will. The charge could be introduced either through the hole at the top or by the door, but it was found that the coke was of much more even density if charged by the door, as when shot in from the top a dense mass of smalls was formed under the hole, which carbonised more slowly than the rest, and so gave a less uniform quality of coke.

In Silesia, ovens of much the same kind were employed; but the top was kept closed, a little air was admitted at the

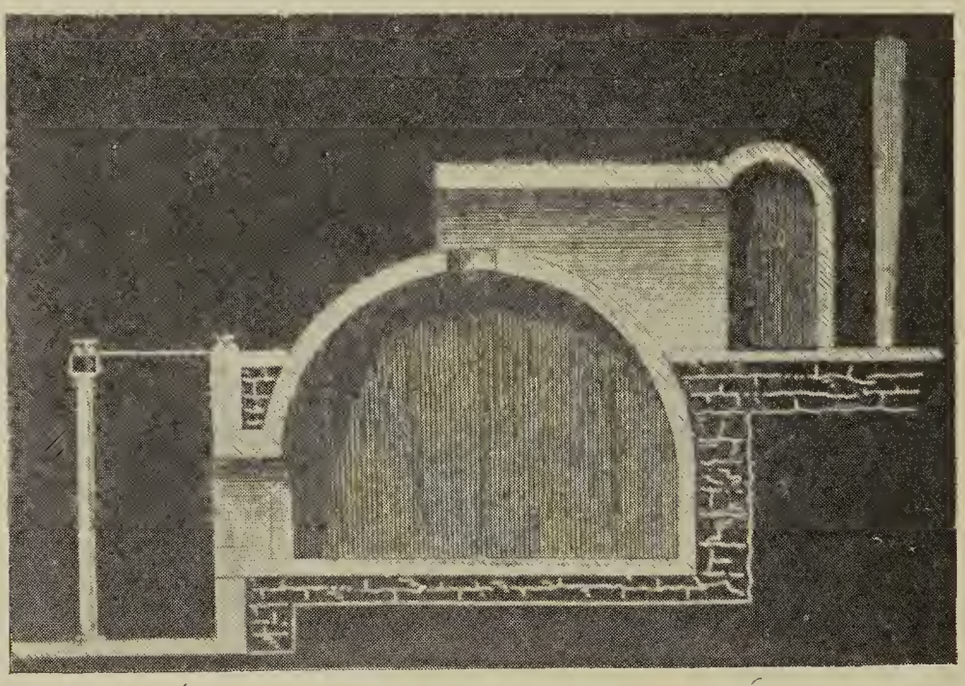


Fig. 18.—Modern beehive oven.

bottom and sides, and the gases and vapours were led by a side tube into a tank of water, where the tar condensed and the gas escaped.

In both these forms of oven the new charge introduced fired from the bottom, if the structure remained hot enough from the last charge, but as soon as the gas began to be evolved it burnt above the charge, and the heat, spreading downwards through the mass, continued the carbonisation, the completion of the action taking eighty-four to ninety-six hours per charge of seven tons. At the end of this period

the top cover was put on, and the oven allowed to cool down for twelve hours. The coke was then drawn by rakes, and quenched with water.

The beehive oven still rules supreme in Durham, Scotland, and America. The latest form utilises a portion of the waste heat; to do which the ovens are built back to back, with a flue between them, the suck of a chimney drawing the hot products of combustion and incompletely burnt gases through

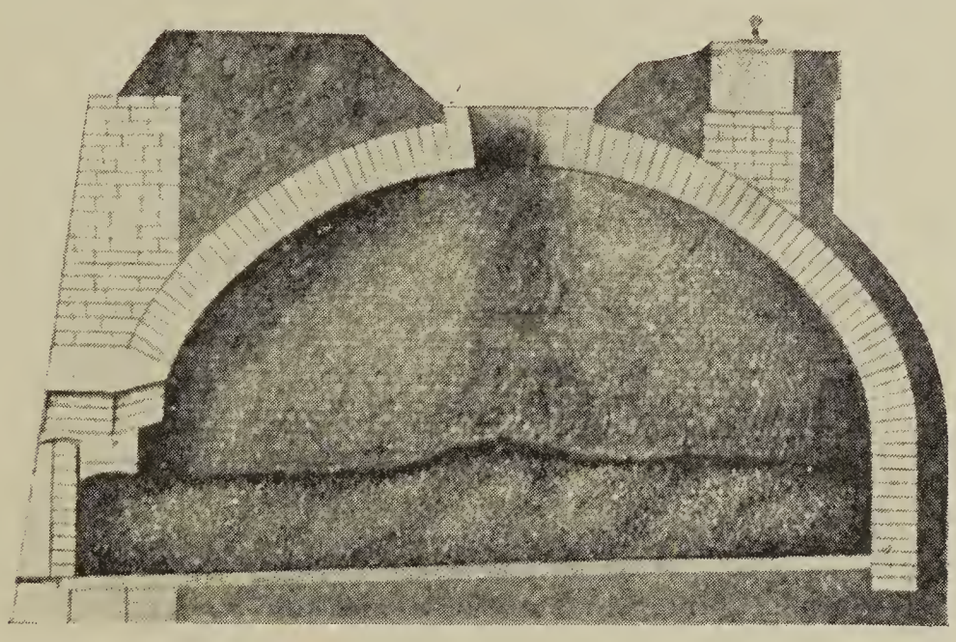


Fig. 19.—American oven.

the furnace space of a Lancashire boiler, and so utilising them for raising steam.

The type most used in America differs but little from the English pattern. The oven is dome-shaped, 12 feet in diameter by 7 feet high. It is charged through the top opening either from a coal trolley running on lines above the opening, or, when the ovens are built back to back, from a top truck running between the top openings of the two rows. The usual charge of coal is six tons, and is fired by the heat of the chamber, after which, the air supply being above the charge and passing in through a regulator above the door, combustion takes place from the top downwards, giving at

the top of the carbonising mass a thick layer of red-hot coke through which the gases from below must pass, and which effectually decomposes any heavy hydrocarbons, with deposition of their carbon. The carbonisation takes from forty-eight to eighty hours, and the coke is quenched before drawing.

In this, as in all other forms of beehive oven, air being admitted to the carbonising mass, it is clear that a certain proportion of the carbon of the solid residue, as well as the gases, must be burned, and the coke yield is rarely more than 60 per cent. of the coal carbonised.

The beehive oven answers so well for certain types of coal difficult to deal with in narrow chambers, that it has retained its pride of place down to the present day, but from time to time attempts have been made to so arrange its construction as to recover some of the valuable products that were not only being wasted, but were ruining the atmosphere and vegetation for miles around.

One of these attempts—for they have all proved abortive—was of special interest, as throwing a side-light on the causes of the superiority of the beehive oven coke. It was made by Jameson in 1883.

As we have seen, in the beehive oven the combustion is downwards. Jameson fitted in the floor of his oven perforated pipes leading to a tap and exhauster, by means of which a downward suction of the distillation products and their withdrawal without passage through the red-hot surface coke could be effected, and the tar and any ammonia from the gas could be recovered. The process, although it attracted a great deal of attention, was not a success, as it was found in practice that the downward suction, by drawing in more air to the crown of the oven, increased the rapidity of the carbonisation and reduced the yield of coke not only in quantity but in quality, so that the net result was a soft coke no better than the product of the gasworks, and very friable, with only a small yield, whilst the tar, being a low

temperature product, was a paraffinoid tar, having many of the characteristics of "coalite" tar, and of very little use for colour production. The interesting point is that the withdrawal of the rich gas and tar should weaken the coke and make it akin to a gasworks coke. This clearly defines the difference between gas-making and coke production.

In gas-making, where illuminating power is essential, small charges in thin layers quickly carbonised in a short time yield the maximum of gas rich in illuminants, but in the coke oven, large charges and long periods of heating give a poor illuminating power but a strong coke, as the carbon from the degradation of the hydrocarbons lutes the mass into semi-metallic hardness.

Many more alterations have taken place in coke ovens than with gas retorts. In dealing with the earlier forms it will be well to adopt some simple form of classification to aid in arranging the various types suggested from time to time in such a way as to show the evolution of the modern ovens.

The first broad sub-division may be into two classes—

1. Internally fired ovens into which air is admitted, and the heat for carbonising is derived chiefly from the combustion of the gas, but partly from the coke.

2. Externally fired ovens to which no air is admitted, and all the heat for carbonising is got from the combustion of the gas.

To the first class belong the meiler heap and its descendant, the beehive oven, which is still the type most largely used; whilst to the second belong all the intermediate ovens that paved the way to the introduction of the modern by-product recovery ovens, chamber and vertical gas retorts.

Many forms of coke oven were introduced in the 'sixties and 'seventies. The two most interesting are the Coppée and the Appolt; the former being the forerunner of the present recovery plant, and the latter of the modern vertical retort.

In the Coppée ovens the carbonising chambers were long and narrow, with sides slightly tapering from back to front, and about 3 feet 6 inches high. Crushed coal was fed into them from the top, and was carbonised by the combustion of the gases evolved from the coal, which escaped through openings in the sides into flues between the chambers, where it met an air supply and burnt, heating the sides of the chamber. The ovens were built in batches and were charged in rotation, so as to equalise as far as possible the heating value of the escaping gas, which is large in volume and high in calorific value during the first half of the carbonising period, and rapidly falls during the second. When the action was completed the coke was pushed out from the oven by a ram, both ends of the oven being closed by doors.

These ovens were introduced at Chapeltown, near Sheffield, in the early 'seventies, and about the same time at Ebbw Vale, and they contain many of the characteristics found in the modern recovery plant ovens.

The Appolt oven consisted of a rectangular structure containing twelve coking chambers or built-up rectangular retorts, having a top section of 3 feet 8 inches by 13 inches, and a bottom section 4 feet by 1 foot 6 inches, and between the chambers, flues varying with the taper of the retorts. Vents in the side walls of the retorts allow the gases and vapours to pass into the flues, where, meeting the air supply, they burn and yield the necessary temperature.

The retorts were fitted with doors at top and bottom, so that they could be fed and discharged by gravity. These ovens were used as early as 1857, in the collieries of the Pas de Calais, and the large heating surface constituted a great advance on any previous form of oven.

About the 'sixties various attempts were made to introduce ovens from which it would be possible to collect some of the by-products, but no very successful result was obtained until about 1879, when Simon and Carvès introduced a

recovery plant in which, taking the Coppée form of oven, they closed the side exits for the gas into the flues, and led it off by a dip pipe and hydraulic main to condensers and scrubbers

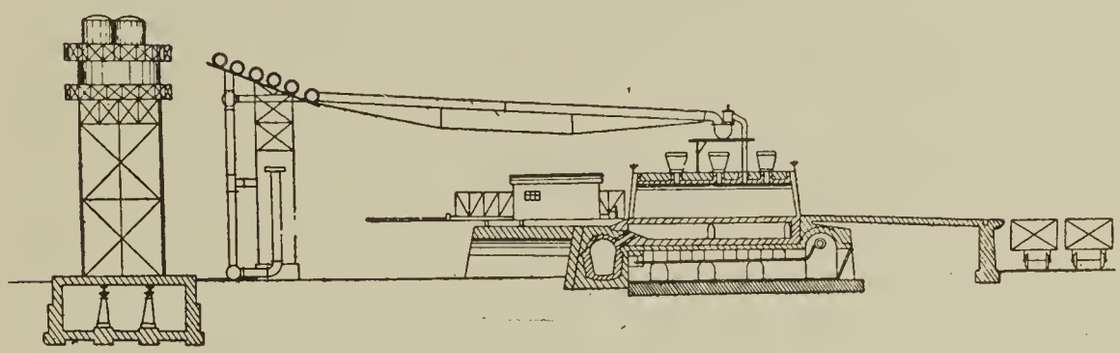


Fig. 20.—Simon-Carvès recovery oven.

which extracted the tar and ammonia, the gas being led back to the ovens and burnt in the flues, to heat the chambers.

Soon after this, ovens of the same character were introduced by Dr Otto, which differ from the Simon-Carvès plant chiefly in the arrangement of the combustion and heating flues, and

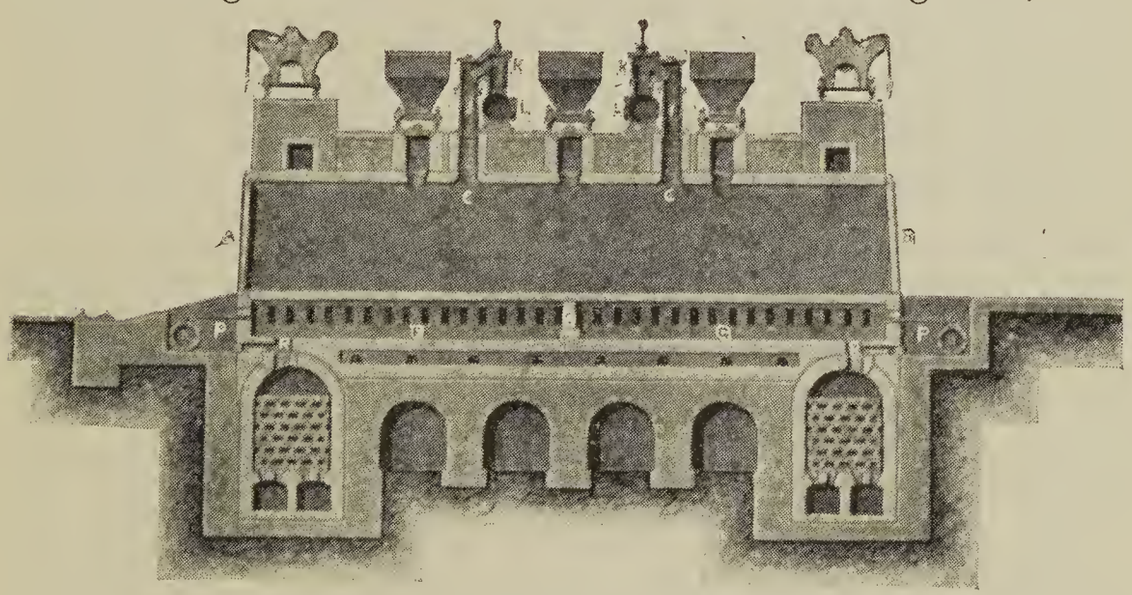


Fig. 21.—Otto recovery oven.

in making up for the loss of heat due to removing, cooling, and scrubbing the gas before combustion, by using Siemens regenerators to extract the heat from the flue gases and highly preheat the air used in the combustion.

During the past thirty years many improvements have

been made in the earlier forms of recovery plant coke ovens, and at the present time only one-half the gas produced in the carbonisation is needed for firing the ovens. This has led to attempts being made to so arrange the working of the plants as to fit them for the production of the gas supply for large towns, the economies incidental to working with large charges offering an important reduction in the cost of coal gas. As soon as the legislature abolishes the absurd trammels that bind the English gas-maker to a standard of illuminating value, which means nothing, and adopts a standard of heating power, which means everything, some advance may be made in this direction in localities where there is a good market for metallurgical coke.

The improvements in the recovery ovens since their first inception have been largely in the arrangement of the flues for heating the sides of the chambers. The superiority of vertical over horizontal flues is now generally admitted, allowing the necessary temperature to be attained with a consumption of less than half the gas produced by the carbonisation.

A great difficulty that was found was to get even and continuous heating of the chamber walls, as when, in the early Hoffman ovens, the Siemens regenerative principle was adopted, the alternate application of heat to only one-half the chamber wall, the heating being alternated every half-hour, gave fluctuations in temperature which affected the carbonisation and strained the brickwork; and the same trouble was found in the United Otto and Koppers ovens.

In his later oven, introduced in 1905, Dr Otto doubled the number of regenerators, so as to reverse alternately in four sections, whilst Coppée in his newest type makes the reversal in five sets out of ten sets of flues, and Collin extends the reversal to alternate flues, thus ensuring the most even temperature.

In 1901 Dr Schniewind read a paper at the International Engineering Congress held in Glasgow, on the production of

illuminating gas from coke ovens, which attracted a considerable amount of attention to this subject, and in it he described the progress that had been made in the United States and Canada in utilising the richest portion of the gas for town supply and the use of the remainder for heating the ovens. Plants for this purpose were erected by the United Gas and Coke Co. at Everett, Mass., Hamilton, O., Camden, N.J., and Sparrows Point, Md., and consisted of an adaptation of the Otto-Hoffman process.

The ovens are in bunches of fifty, which form the unit. Each oven consists of a gas-tight chamber 43 feet 6 inches long, 17 inches wide, and 6 feet 6 inches high. The ovens are erected side by side, and are separated by hollow walls divided into ten compartments, each containing four vertical flues, directly under which are the combustion chambers, with an air chamber below the retort. The air is regenerated to 1800° F. (982° C.) by a pair of regenerators under the centre of the battery and running its entire length, from which the air is conducted to the chamber below the retort, and, meeting the gas in the combustion chamber, burns upwards through the flues. It is claimed that this construction gives a uniform distribution of heat throughout the setting, and also allows the brickwork to be inspected easily in every part. The regenerators are of the Siemens type, and are reversed every thirty minutes, and the products of combustion ascend through the vertical flues to a horizontal flue above, and after passing down and through the regenerator are led off to the chimney stack.

The arrangements for coal handling are of the usual type. The trucks drop the coal into a store, from which the elevators feed a large bin over the chambers. Between the store bin and the chamber a space is left, in which a long trough or bin runs on a track and is fitted with eight feed spouts in the bottom. The trough having been filled from the bin it is run by an electric motor over the chamber to be charged,

and the charge is shot in through holes in the crown of the oven. If very dense coke is required, it can be obtained by compressing the coal into a sheet iron mould a little smaller than the retort, and pushing it in by means of a ram through the oven doors.

When carbonisation is completed the oven doors are raised, and the coke, weighing about six tons, is pressed out by a movable ram on to a tilting platform, by which, after quenching with water, it is fed into trucks.

Each chamber is connected at the top with two mains which run the entire length of the bench, one being at each end of the chamber, and during the carbonisation the rich gas given off during the first period is run off by the "rich gas" main, whilst that from the latter period is taken by the "poor gas" main. Both fractions of gas undergo the same sequence of treatment as regards cooling, tar, and ammonia extraction, but after that point the rich gas is purified and goes to the holder for distribution, whilst the poor gas passes out into the benzol scrubber where the benzol is extracted by tar oil, and the gas returned for combustion in the carbonising plant.

The actual working results at Everett Dr Schniewind gives as follows :—

	Per Ton.		
	Rich gas for distribution.	Poor gas for heating ovens.	Total.
	4448 cubic feet.	5560 cubic feet.	10,080
Illuminants . .	5·0	2·5	
Methane . . .	37·4	29·2	
Hydrogen . .	44·3	51·8	
Carbon monoxide .	6·2	5·0	
Carbon dioxide .	2·9	2·0	
Oxygen . . .	0·1	0·4	
Nitrogen . . .	4·1	9·1	
Calorific value B.Th.U.	707·8	515·0	
Candle-power . .	17·4	8·0 CO_2 free	

The distribution of the heat of the original coal amongst the products is given as follows :—

100 lbs. of dry coal yield—	B.Th.U. per lb.	Total calorific value.	Per cent.
71·13 lbs of coke . .	12,645	899,456	72·3
3·38 lbs. of tar . .	12,210	51,410	4·1
229 cubic feet of rich gas .	686	157,504	12·7
234 cubic feet of poor gas	567	132,835	10·7
Ammonia liquor, sulphur and loss . . .		2,496	0·2
100 lbs. dry coal contain B.Th.U.		1,243,700	

So that the carbonisation of the coal is carried out with an expenditure of only 10·7 per cent. of the heat value of the coal, which is equal to the best continuous vertical retort practice, and considering that the carbonising period is twenty-nine to thirty-four hours is a wonderful result.

The coal used at Everett was Dominion coal, which is a very good gas coal.

Since 1901 many plants of this character have been erected in America, the period of carbonising has been reduced to about twenty-four hours, and the system may be looked upon as firmly established in American practice. It is interesting, therefore, to examine from an impartial point of view the differences between the American coke oven processes and the Continental gas chamber processes, and why it is that there seems to be no burning anxiety at present to adopt either in England.

There is nothing more interesting to the outside observer than to watch the attitude taken by those controlling the destinies of our great industrial manufactures towards new ideas, and the desire they show to cling to the letter of the methods which in the past have led to success, forgetting that outside circumstances influence the laws of supply and demand quite independently of their methods of procedure.

From the first inception of the recovery oven in England its history has been one of struggle against prejudice. All the time it consumed its own gas it had to fight the consumers of furnace coke, who alleged its produce was inferior to beehive coke, and now that the iron-founder has wearied of paying extra for his pet fuel and admits that recovery oven coke is every whit as good or a bit better, the trouble arises that the recovery oven plant has been so improved that one half the gas suffices to do the carbonising work, and the more conservative members of the gas industry are obsessed with the fear that it may become a rival, and that the gas-managers' by-product market may be injuriously affected, a feeling which makes it difficult for the recovery oven advocates to get an impartial judgment formed on their claims.

Taking first the differences between chamber carbonisation and the by-product recovery gas oven, we find that from considerations of economy, due to dealing with large bulks of material, the chamber gas-maker and the coke oven manager have both come to what is to all intents and purposes the same form of apparatus, worked under the same conditions of temperature and for the same time, and the whole difference between the two is that the gas manager, with his mind fixed on making the largest volume of gas, collects and distributes the whole of it, burning part of his coke in outside producers to obtain the heat in his setting; whilst the coke oven manager is bent on the largest yield of coke, and so obtains the necessary temperature by burning the poor coal gas that is evolved during the second half of the period of carbonisation, a procedure which, when a high candle-power gas and metallurgical coke are the desired products, is undoubtedly right, but which, I think, is wrong when fourteen candle-gas and domestic fuel are the things we need. I have made my opinion already as to the chamber carbonisation for the purpose clear—if it ever is to succeed in England, it

will be only after enactments as to candle-power have been swept away.

By far the best statement of the claims of the by-product recovery gas oven as a process for the manufacture of illuminating gas was made by Ernest Bury, in his paper before the Institution of Gas Engineers in 1907, the great value of the paper depending largely on the absolutely fair way in which he states the drawbacks as well as the advantages of carbonisation in bulk. From his long experience in coke oven management and his scientific knowledge, he is probably better fitted to speak than any authority in England, and he freely admits that the by-product coking chamber, from its method of construction, from the large end doors which can be made only partially tight by luting, and from the length of the period of carbonisation, is more liable to serious leakage both of gas outwards and air inwards than any other system. Also, that the high temperature in the top of the chamber, which is always above that of a gas retort, and the abnormally high temperature at the time when the charge is fed in, are all facts that at first sight appear to condemn the chamber and oven processes as methods for making gas as compared with the gas retort, but that in spite of these drawbacks the economies are so great that the cost of a 540 B.Th.U. gas at the pit head would amount to only 4d. to 5d. per thousand cubic feet, or less than half the cost at our big London works.

I agree entirely with Mr Bury that if the gas supply of the country could be made at the pit's head, and the gas supplied under pressure through trunk mains, large economies would be possible, but it is the coke side of the question that seems to me to be the insuperable objection. In America the by-product oven is a success because long ago they had the sense to abolish bituminous coal as a domestic fuel, and it is high-priced anthracite and not cheap bituminous coal that the coke has to compete with, and as metallurgical coke

is a fuel that answers perfectly in the closed anthracite stoves it follows naturally that the domestic fuel market is open to it. In England, however, with our open fire grates, often with hardly enough draught to burn bituminous coal, and needing an easily ignited and free burning fuel, such coke would have no chance of success, and this so alters the whole position that one has to admit that carbonisation in bulk can succeed only in those districts where metallurgical coke is a necessity.

CHAPTER V

THE CONDITIONS EXISTING IN THE DESTRUCTIVE DISTILLATION OF COAL

Vapourisation—The effect of temperature on matter—Destructive distillation—Heat of formation—Exothermic and endothermic compounds—The work of Euchêne on the heat of formation of coal—Mahler's determinations—Researches of Constam and Kolbe on the calorific value of coals and their distillation products—Specific heat—Heat used in the distillation of coal—Economies possible—Rate of conduction of heat through walls of retort—Temperature of carbonisation—Ratio of heating surface to weight of charge—Co-efficient of conductivity of fireclay—High and low temperature carbonisation—Passage of heat in vertical retorts, chambers, and transmission of heat through ordinary charge in horizontal retorts and through fully charged horizontal retorts—The improvements obtained by using fully-charged horizontal retorts—The theories of the cause of the improvement as stated by Bueb, Ste Claire Deville and others—Temperature of charge in Dessau retort—Effect of the size of coal on the escape of the gases—Fracture of coke from horizontal retorts and coke ovens—The swelling of coal—Temperature of gas from mouthpiece of an intermitten vertical retort—Effect of pressure on the gases given on distillation—Size of coal an important factor in securing uniformity of gas—Auto-carburetting—Blass' experiments.

All solids and liquids which do not decompose below their boiling point can be converted by the action of heat into vapours. This is dependent upon the fact that all substances are built up of extremely minute particles, which are termed "molecules," and which on heating repel each other.

If we take a bar of zinc at the ordinary air temperature and carefully determine its size, and then heat it, we find that the action of heat is to cause it to increase in bulk, this

increase proceeding at a definite rate until we have raised the temperature to 423° C. (793° F.) when it becomes liquid. If, now, the liquid be further heated, it will be found to still continue to expand until a temperature of 1040° C. (1904° F.) is reached, when it boils like water, and is converted into the gaseous state.

During this alteration in volume and final conversion into vapour the work which the heat is doing in spacing asunder the particles is, in the first place, to reduce the force of cohesion, which in the solid state holds them rigidly together, and so to endow them with the mobility of the liquid state ; whilst the still greater spacing apart that takes place when the liquid is heated to its boiling point entirely does away with cohesion, and each particle is free to move independently, and gives us the vapourous or gaseous condition.

If, now, the heat which has performed this inter-molecular work is again absorbed from the gas or vapour, the latter condenses to the liquid state, and with a further removal of heat from the liquid the solid is once more produced.

An action of this character, in which merely by the aid of heat a solid or liquid is converted into a vapour which can be condensed by cooling again to the original substance, is called one of "distillation," and if the body which is distilled decomposes at the temperature necessary to convert it into gaseous matter, so that the products cannot be again condensed into the original substance, it is termed "destructive distillation." The effect of heat upon coal is to decompose it into the solids which remain behind in the retort, the liquids which condense in the hydraulic main, and the gaseous products.

In considering the actions taking place during the destructive distillation of coal we are met at the outset by the difficulty that little or nothing is known as to the heat of formation of coal.

When two substances combine together under ordinary conditions heat is evolved, and the compound is called "exothermic," and when this compound is again broken up, as much heat has to be poured into it as heat or in some other form of energy as was given out during its formation. A few bodies are known, acetylene being one of them, which instead of giving out, absorb heat during formation; these bodies are called "endothermic," and when once decomposition has started the heat of formation is again given out, and in many cases adds to the rapidity of decomposition.

Now it is well known that some hydrocarbons are like acetylene of an endothermic character, and coal itself has been suspected of possessing this property.

Amongst the bodies formed by the destructive distillation of coal, some liberate heat in their formation, whilst others absorb it. These bodies may be tabulated as follows:—

Bodies formed with Liberation of Heat
(exothermic)

	B.Th.U. per lb.
Carbon dioxide	+ 14,646
Carbon monoxide	+ 3,223
Methane	+ 2,417
Water	+ 62,100
Sulphuretted hydrogen	+ 243
Ammonia gas	+ 1,290

Bodies formed with Absorption of Heat
(endothermic)

	B.Th.U. per lb.
Benzene	− 107
Ethylene	− 797
Carbon disulphide	− 739
Cyanogen	− 2374
Tar vapour	− 540

The determination of the heat of formation of a body like coal is one fraught with the greatest difficulty, for it is evident that, as the composition of coal in a mine will vary not only in different seams but even in the same seam, there is no definite composition, and that nothing can be known as to the heat of formation except by direct determination, which necessitates experimental estimations of so complicated a nature that the introductions of error is extremely likely to vitiate the results.

Probably the most valuable work done in this direction is to be found in a report presented by M. Euchêne, on the thermic reactions which occur during the distillation of coal, published in the *Transactions of the International Gas Congress in Paris*, 1900, in which he determines the thermo-chemical data coming into play during the distillation of coal in the manufacture of gas, with careful estimations of the heat of formation of the products of the distillation as compared with the heat developed by the fuel needed for the distillation ; that is to say, a balance is struck, showing on the one side the heat generated and on the other the heat expended, the difference found representing the heat of the decomposition of coal.

M. Euchêne has determined in this way the heat liberated during the distillation of three types of coal, these results showing in a striking way that the heat liberated increases in nearly regular ratio with the amount of volatile matter in the coal, and that the more oxygen the coal contains the more endothermic its reaction, a fact which points clearly to its being the oxygen-bearing compounds in the coal which give it its endothermic character.

M. Euchêne in his experiments obtained results which may be tabulated as follows :—

Moisture.	Ash.	Carbon.	Hydrogen.	Oxygen.	Volatile matter.	Heat of formation calories.	B.Th.U.
2·70	7·06	77·56	4·79	5·94	25·99	+ 12·39	22·3
3·31	7·21	76·00	4·78	6·82	28·30	+ 35·98	64·7
4·34	8·18	72·08	4·78	8·73	32·17	+ 63·51	114·3

At an earlier date, 1893, Mahler determined the calorific effects of distilling a coal of the same composition as the one from which Euchêne obtained 63·51 calories (114·3 B.Th.U.), and did so by experimentally determining in his bomb the heat value of the coal and of all the products of distillation, and found that the former exceeded the latter by 254·8 calories (458·7 B.Th.U.). It is quite clear, however, that in the determination of a factor of this kind, which is dependent upon the difference between two figures obtained from a highly complicated set of determinations, each with its own source of error and all tending in the same direction, these will be borne by the resultant, and it is not surprising, therefore, to find that with a coal of the same type these two observers found a substantial difference.

In Mahler's work the resultant was arrived at by deducting the heat of combustion of the products from the heat of combustion of the coal, whilst Euchêne's determinations were obtained by taking the difference between the heat supplied and the heat consumed during distillation, so that the difference between these two would be likely to be increased by errors leading in opposite directions.

More recently, in 1909, Constam and Kolbe made a very able research upon the carbonisation of typical English coals, and determined their calorific value and also the calorific value of their distillation products, and found that the value of the coal exceeded the heat value of the products to the extent shown in the following table, in which the heat balance of the products of distillation of the ash-free and dry coal is given in percentages of the heat value of the coal substance:—

Description of coal.	Heat found in—				Loss of Heat.
	Coke.	Gas.	Tar.	Pitch.	
I. Nottingham, bright coal	61·3	22·7	8·4	1·6	6·0
II. Lancashire, Trencherbone	61·7	22·8	11·0	1·4	3·1
III. Nottingham, best hard .	64·1	20·2	10·0	1·3	4·4
IV. Kinneil . . .	62·9	22·0	9·5	2·1	3·5
V. Durham, Low Main Seam	63·7	20·6	9·5	2·2	4·0
VI. ,, Hutton . .	65·3	22·1	7·7	2·0	2·9
VII. Yorkshire, Barnsley .	70·4	18·3	6·9	1·9	2·5
VIII. Durham, Ballarat .	73·6	18·6	2·5	1·7	3·6
IX. Welsh, Nixon's Navigation	76·7	16·9	2·9	1·4	2·1

This shows, as in the other determinations given, that when we get down to a steam coal, *i.e.*, a coal poor in volatile matter and oxygen, its calorific value approaches more nearly that obtained by calculation or by determination of the heat present in the products.

If we now take the Low Main, Barnsley, and Hutton seam coal and calculate what the loss of heat shown in the above table amounts to per lb.—of ash- and water-free coal—we obtain the following results :—

	B.Th.U. per lb.	Loss per cent.	B.Th.U.
Low Main .	15,393	4	615·68
Barnsley . .	14,792	2·5	369·80
Hutton . .	15,766	2·9	457·21

And the average of these results would be 480·9 B.Th.U. per pound. If we take this as due to the endothermicity of the coal, the figure agrees fairly well with Mahler's determination.

The evidence with regard to the endothermic character of coal is not of a very satisfactory nature, and I think that the strongest proof that it probably is endothermic when the coal contains a large proportion of humus body is that cellulose, lignose, and peat undoubtedly show an evolution of heat during their decomposition, this being due to the

rearrangement of the oxygen present with formation of highly exothermic compounds, as was shown by Ramsay and Chorley's researches upon the decomposition of wood and cellulose, to which reference will be made later on.

When a coal is carbonised it decomposes into gases and vapours, leaving behind in the retort the solid coke, and heat is used up in the decomposition in the change from the solid to the gaseous form, and in raising the gases and vapours to the temperature of the retort.

The amount of heat needed to raise a unit weight of any form of matter through one degree is called its specific heat, but the specific heat of gases ofter is found to vary considerably as the temperature rises, so that it is impossible to say from the specific heat of a gas taken under ordinary conditions what its specific heat will be at high temperatures.

Mallard and Le Chatelier made a number of experiments upon this point, from which the following table was deduced by Euchêne :—

B.Th.U. needed to raise One Cubic Foot of Gas to given Temperature

	1050° C. 1922° F.	975° C. 1787° F.	800° C. 1472° F.	650° C. 1202° F.
Nitrogen, Oxygen, Hydrogen, Carbon monoxide	38·8	36·0	29·2	23·6
Steam	113·6	108·4	96·4	86·8
Carbon dioxide	68·8	62·4	48	37·2
Methane	..	..	..	45·2
Sulphur dioxide	102·8	97·6	85·0	71·0
Benzene	..	..	..	145·6
Cyanogen, Carbon disulphide, Sulphretted hydrogen, Ammonia	..	..	..	44·0
Tar	..	..	..	761·4 per lb.

Of these temperatures 650° C. (1202° F.) is the important one, as this may be taken as the temperature of the gas in the retort.

For each 1 lb. of coal decomposed in the retort the heat used up in the decomposition and distillation amounts to 462 B.Th.U. over and above the heat due to endothermic reactions. The heat withdrawn from the retort by the hot gas and vapours amounts to 324 B.Th.U., and the heat in the red-hot coke when it is drawn accounts for another 442 B.Th.U., so that the heat that has to be actually supplied for the carbonisation is 462+324+442=1228 B.Th.U.

The losses in the setting, however, exceed this, and in an ordinary horizontal bench would be 1463 B.Th.U. escaping with the flue gases, 398 B.Th.U. lost to the air by radiation and convection, and 25 B.Th.U. in the ash, making in all 1884 B.Th.U.

The thermal value of the reactions in the retort will remain the same whether the distillation be carried out in a horizontal, vertical, or inclined retort, in a coke oven or a chamber, and it is chiefly in the setting that the economies have been made which reduced the carbonising fuel to the figures attained in modern practice.

In the horizontal retort setting quoted above the total heat used would be 1228+1884=3112. Now, 1 lb. of gas coke gives an average of 14,200 B.Th.U. in its combustion, so it would give enough heat to carbonise 4·5 lbs. of coal, or, in other words, the coal would require 21·9 per cent. of its weight of coke to carbonise it, whilst if the whole of the heat of combustion could be used in the retort 8·6 per cent. would be sufficient.

A fair idea of the economies that are possible can be obtained by stating the heat used in the setting and retort in percentages :—

		B.Th.U. per lb.	Per cent. of heat used.	
Used in retort	1. Decomposition and distillation .	462	15·7	39·3
	2. Escaping in gas and vapours .	324	10·4	
	3. In hot coke .	442	13·2	
Lost in setting	1. Flue gases . .	1463	47·2	60·7
	2. Radiation and convection . .	398	12·8	
	3. Ash . . .	23	0·7	

so that 39·3 per cent. of the heat is used in the retort, and 60·7 in the setting, the item which overshadows all others being the 47·2 per cent. which escapes up the chimney in the hot flue gases.

It is evident that the first step towards economy is to be found in a better utilisation of the heat in the setting, so as to abstract as far as possible the heat from the products of combustion, and this is done by regeneration, which reduces the flue gases by over 300° C. (572° F.) in temperature, and brings down the loss due to this item from 47·2 to 25·2 per cent., whilst feeding the producers with red-hot coke from the retorts effects a further economy, with the result that the fuel used falls from 21·9 to 14·8 per cent. and even lower.

Under these conditions the percentage of heat used in doing the work of carbonisation would be largely increased, and the chart would be as follows :—

Used in retort	1. Decomposition and distillation . . .	21·4	54·1
	2. Escaping in gas and vapours	13·8	
	3. In hot coke . . .	18·9	
Lost in setting	1. Flue gases . . .	25·2	45·9
	2. Radiation and convection	19·9	
	3. Ash	0·8	

So that over one-half the heat is utilised in work.

In the Glover-West vertical retort a still further reduction in the fuel used is obtained by cooling the coke in a chamber at the bottom of the retort, and utilising the heat to raise the temperature of the secondary air supply, this bringing the fuel consumption down to 10·4 per cent.

Mr D. D. Barnum read a paper before the New England Gas Association on the "Thermic considerations of a retort furnace," in which he gives a balance-sheet for a bench of six retorts, and in which 17 lbs. of coke were used as fuel per 100 lbs. of coal carbonised. The results of his tests were :—

Expended	B.Th.U.
Heat from Coke . . .	215,623
Heat of Formation (plus) .	37,992
Total . . .	253,615

accounted for as follows :—

	B.Th.U.	Per cent.	Per cent.
Carried up chimney as gases	38,855	35·0	47·6
,, ,, water .	31,943	12·6	
Lost in ashes	..	*nil*	
Carried off by gas . .	15,503	6·1	9·2
,, ,, tar	4,070	1·6	
,, ,, water . .	3,759	1·5	
Radiation and convection .	20,931	8·3	
Hot coke . .	33,708	13·3	
Heat of formation . . .	3,267	1·3	
Balance . .	51,579	20·3	

The net heat of decomposition would be 51,579 −37,992 +3267=16,854 B.Th.U. or 6·6 per cent. ; and this is the heat of decomposition furnished by the coke in the furnace over and above the heat of formation furnished by the coal in the retort. It will be seen that the percentages of heat used and lost do not differ very widely from the figures already given.

In the days of the old iron retort there was no trouble as to the rate at which heat could be poured by conduction through the walls of the retort and into the charge, but when the fireclay retort took its place, the introduction of a two to three-inch wall of a material having only about one-tenth the conducting power of the iron seemed at first a serious difficulty. It was soon found, however, that the slow conductivity of the mass made it an effective storage material for the heat, and that when in properly constructed settings the flues and brickwork surrounding the retort had attained their maximum temperature, they provided a reserve of heat which not only neutralised the slow conductivity of the mass but also helped to level up the rate at which the heat was supplied to the retort.

The conduction of heat through a substance like the walls of a fireclay retort is a determination fraught with many troubles, as the conditions existing in a retort heated in a bench are totally different from those that can be obtained in making experimental determinations in a laboratory. In any calorimetric determination the one side of the test piece is continuously cooled by the calorimeter, whilst the heat poured into the other side is very different in effect to the mass of heated material existing in the flues surrounding the working retort.

The rate at which heat is transmitted under working conditions depends upon the degree of heat in the flue and outer walls of the retort, the higher the temperature the more rapid being the transmission, whilst the difference between the temperature of the outer and inner skin of the retort is a factor of the greatest importance. The greater the difference, *i.e.* the cooler the inner skin and the mass in contact with it and the hotter the outer skin in the flue, the more rapidly will the heat pass. Again, the rapidity of transmission varies with the character of the fireclay, with its porosity, and with the temperature and length of

time for which it has been baked; so that it is impossible to give any definite figure as to the rate of conductivity or transmission which shall hold good in all cases. Determinations based upon the rate of transmission at comparatively low temperatures may be discarded at once as valueless, but Dr G. Beilby determined the conducting power of firebrick, and came to the conclusion that one square foot of firebrick, one inch thick, passed 6·59 centigrade pound units, or 11·86 B.Th.U. per hour for each degree centigrade of difference between the sides of the brick, when these differences were of the magnitude of 200°-300° C. (392°-572° F.).

My own opinion is that at the ordinary working temperature of a retort under gasworks conditions the amount of heat transmitted approximates to 25 B.Th.U. per square foot of surface for each 1° C. difference in the temperature of the outer and inner surface of the retort, and that this is not seriously affected by the thickness of the fireclay, as conduction is so slow with a retort 3 inches thick that it is probably only the internal portion that is cooled to any great degree when a fresh charge is fed into a properly heated retort, and the mass of fireclay acts as a store of heat, so that the heat has only a short travel.

In a horizontal retort ready for charging the temperature of the inner walls will approximate to 1000° C. (1832° F.), and the flue temperature to 1100° C. (2012° F.), and the fireclay walls of the retort will conduct the heat at a rate which approaches to 25 B.Th.U. per square foot per hour for each degree centigrade difference in the two surfaces, so that during the first two hours, when the average temperature of the inner side of the retort walls, cooled by the charge and by the retort having been opened, will not be more than 800° C. (1472° F.), the amount of heat passing through the walls into the charge will be—

$25 \times (1100 - 800) = 7500$ B.Th.U. per square foot of surface,

whilst by the fifth hour, when the inner side of the wall of

the retort has risen to 950° C. (1724° F.), the amount passing will be—

$$25 \times (1100 - 950) = 3750 \text{ B.Th.U.},$$

or only half the amount passing in the earlier period, the average being approximately 5625 B.Th.U. per hour; which, taking the heat units needed for the actions taking place in the retort as 1228 B.Th.U. per lb., gives a carbonising value for a six-hour charge of twelve tons per 1000 square feet of retort surface.

There is no doubt as to the fact that the heat transmitted by the walls of the retort rapidly falls as the interior heat rises, so that through the whole period of carbonisation the rate of transmission diminishes, whilst the temperature of the charge increases.

Euchêne determined experimentally the proportion of the total heat transmitted by the walls of the retort during a four-hour charge, with the following result :—

1st hour	43·8 per cent.
2nd ,, ...	20·6 ,,
3rd ,, ...	18·7 ,,
4th ,, ...	16·9 ,,
	100·0 ,,

The ratio of heating surface to weight of charge is one of the most important factors in determining not only the rate of carbonisation, but also the composition of the gas. Where large volume and high illuminating power are the desiderata, as has been the case in the past, large heating surface, small charges, and quick carbonisation have yielded the best results, and the horizontal retort, as shown by the foregoing calculation, has given a carbonising duty of twelve tons per 1000 square feet of surface for six-hour charges, a figure which is a little below that given by Mr Bond in his 1905 paper before the Institution of Gas Engineers, who gives

2·13 tons per 1000 square feet per hour. But directly the size of the charge is increased and the ratio of surface decreased, the amount carbonised per hour falls so rapidly that, as Mr Bury has shown, in a coke oven using the same coal the duty is only 0·55 tons per 1000 square feet per hour.

It is clear that there are several factors bringing about this result. In the first place, with the horizontal retort a large proportion of the heating surface is in the bottom of the retort, and side heat is reduced to a minimum, so that convection aids conduction, and the thin layer of coal is carbonised in the quickest possible time. In the coke oven the conditions are reversed, and the whole of the heat has to be laboriously conducted into the charge through thick masses of non-conducting material, and the same applies to the smaller charge in the intermittent vertical retort to, of course, a less extent, so that on theoretical grounds they should carbonise a less weight of coal per 1000 square feet than the horizontal does.

Another important factor acting in the same direction is the influence of the heat of the wall of the retort on the rate at which the heat can be poured into the charge from the flues. The larger the charge the longer has to be the period of carbonisation, and the longer the period of carbonisation the greater the period over which the temperatures of the two sides of the retort walls are within a few degrees of each other and the minimum of heat is passing. In an intermittent vertical retort, the charge takes twelve hours to work off, and during the first period the maximum amount of heat is passing, whilst after the fifth hour this is reduced, and by the seventh hour probably reaches a minimum :—

1st	hour	$25\times(1100-800)$	=7500 B.Th.U. per square foot.
2nd	,,	$25\times(1100-950)$	=3750 ,, ,,
7th	,,	$25\times(1100-1000)$	=2500 ,, ,,

In the continuous vertical retort, on the other hand, the

constant passage in of the cold charge keeps up the difference in temperature of the two sides of the walls of the retort and allows a maximum passage of heat, so that although there is no direct bottom heat to help the rate of carbonisation, the time is brought down to within an hour of the horizontal.

Wologdine has determined the conductivity of refractory materials in connection with their porosity and permeability, and comes to the conclusion that the heat conductivity of bodies like fireclay depends not only on the quantity of contained air, that is, their porosity, but also on the degree of isolation of the gas so contained, that is, on the permeability of the material to gases.

As a general rule it may be taken that the higher the temperature at which the refractory clay has been burnt the smaller is its porosity and the better its conductivity. Some cases, however, occur, as with silica bricks, in which the porosity is but little affected by the temperature of burning, and in these cases the conductivity is also but little altered.

With ordinary fireclay burnt at 1922° F. (1050° C.) the coefficient of conductivity is 1·07, which is increased to 1·81 when the fireclay is burnt at 2372° F. (1300° C.). This explains why an old retort, as long as it is sound, will give better carbonising results than a new one.

It has become the custom to speak of the temperature of carbonisation being high merely because the temperatures in the flues and in contact with the walls of the retort are high, and to speak of the products of high temperature distillation as if the coal had been carbonised at the temperature existing on the retort surface.

It is quite clear, however, that, coal being a bad conductor of heat and coke a worse one, it is only the layer of probably less than an inch thick that is carbonised at anything like the retort temperature, and that the remainder of the charge is distilled at a slowly rising temperature, which attains

its maximum only after the volatile products have been practically all driven off.

The real distinction between high heats and lower flue temperature is that the higher the temperature employed the thicker and hotter will be the layers of coke which the gases and vapours have to traverse in their escape from the inner portions of the charge, and the greater will be their exposure to radiant heat and contact with the highly heated surfaces of the retort in their outward passage from the carbonising mass. The products of the primary action are, in fact, being subjected to secondary decomposition under conditions we neither know nor can control ; and this is one of the weakest points in our methods of carbonising for the production of illuminating gas.

We make elaborate tables of the composition of gases and tars produced at various distillation temperatures, but the only information that they give us is what is left undecomposed under unknown and varying conditions, the only certain factors being that the heat was nowhere above that which we are pleased to call the temperature of distillation.

It is evident that if these variations exist in the temperature at which the coal is distilling in the comparatively small charge in the gas retort, they must be accentuated when one comes to deal with carbonisation in bulk as practised in oven and chamber settings, as not only is the travel of the gases and vapours through the red hot coke much longer, but the rate at which the heat is conducted through the carbonising mass becomes slower as the bulk of the charge increases, whilst the temperature in the crown of the oven during the first half of the time is higher than is found in the gas retort. This also applies to the temperature in the top layers of the coke.

If the coal is carbonised in a 6-inch diameter tube filled so that the heat shall be penetrating from every side, there is an almost immediate rise in temperature throughout the mass, owing to the hot gases and vapours passing through

the interstices between the pieces of coal, and the coke attains its maximum temperature at the rate of about one inch per hour, so that in three hours, with a wall temperature of 1000° C. (1832° F.), the centre of the mass would be at about 950° C. (1742° F.), and the carbonisation would be finished. If, however, the tube be increased to 12 inches in diameter the rate of conduction is reduced to 0·5 inch per hour, and the same thing takes place with a flat chamber retort heated from the sides, so that it would take about twelve hours to complete the carbonisation; whilst with further increase in the width of the chamber the rate of travel of the heat grows still less, the passage of the heat being still slower as the distance between the walls of the chamber gets greater.

The result of this is that in by-product recovery coke ovens and large chamber retorts the period of carbonisation becomes very long, and the gas has to pass through so much hot coke that the illuminating power is reduced to from nine to ten candles.

These rates of passage of heat apply only to vertical retorts or chambers, the sides of which are heated, as bottom heat penetrates the mass rather more quickly, owing to convection coming to the aid of conduction, and the upward flow of heated gases raising the temperature in advance of the conducted heat.

Moreover, the rate at which the heat travels in the carbonising mass depends to a great extent on the initial temperature employed, the figures given being attained only when the flues and outer walls of the retort or chamber are heated to about 1100° C. (2012° F.). If the flue temperature is lowered the transmission of heat becomes slower, and a longer period therefore is required for the complete carbonisation; so that if in a 6-inch tube with a wall temperature of 1000° C. (1832° F.) it takes three hours to complete carbonisation, it would take six hours to do the same work with a wall temperature of

500° C. (932° F.). Consequently, in making low temperature coke, such as coalite, in tubular retorts $5\frac{1}{2}$ to $6\frac{1}{2}$ inches diameter, it takes four hours to drive off two-thirds of the volatile matter that is in the coal.

The temperature of the coke or coal through which the gas and tar vapours have to pass, and the length of travel they have in reaching the exit from the retort or chamber in which carbonisation is proceeding, are two of the most important factors in determining their decomposition, as it is these

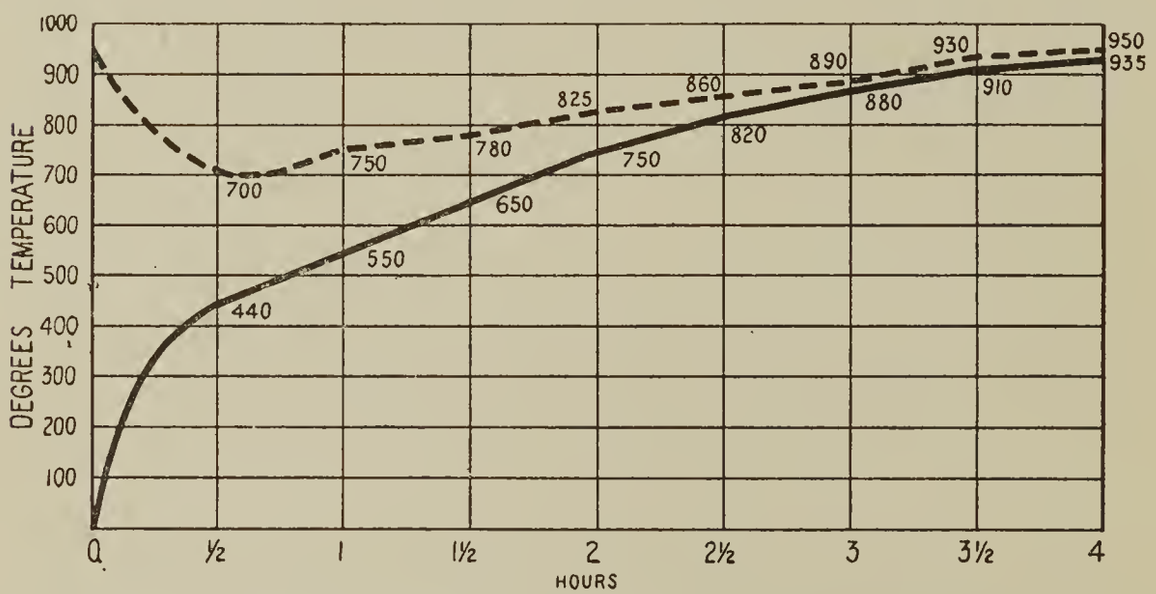


Fig. 22.—Rise of temperature during carbonisation in space above coal.

which give rise to the secondary reactions that largely determine the final composition of the gas and tar.

Many attempts have been made to trace the passage of heat through the charge of coal in a retort, and Euchêne, in the research already referred to, did so by placing Le Chatelier thermo-couples, one in the centre of the charge, and one in the space above it at 14 inches and 4 feet from the mouth of the retort, and from their indications prepared the following two diagrams.

Valuable pyrometric observations on the temperatures existing in charges of varying size have also been made by Mr Bond, of Southport, and other observers, from whose work we can deduce the following results as typical.

If an ordinary ⌓-shaped horizontal retort, 18 to 20 inches wide and 15 inches high, has a 6-inch charge fed into it, the space from the apex to the crown of the top of the charge will be 9 inches deep. If now thermo-couples properly protected are placed (1) at the bottom of the charge, (2) in the centre, and (3) at the top of the charge, we can gain a good idea of the way in which the heat is acting on the coal.

With full heats the coal at the bottom of the retort rapidly heats up, and in fifteen minutes has reached 700° C. (1292° F.),

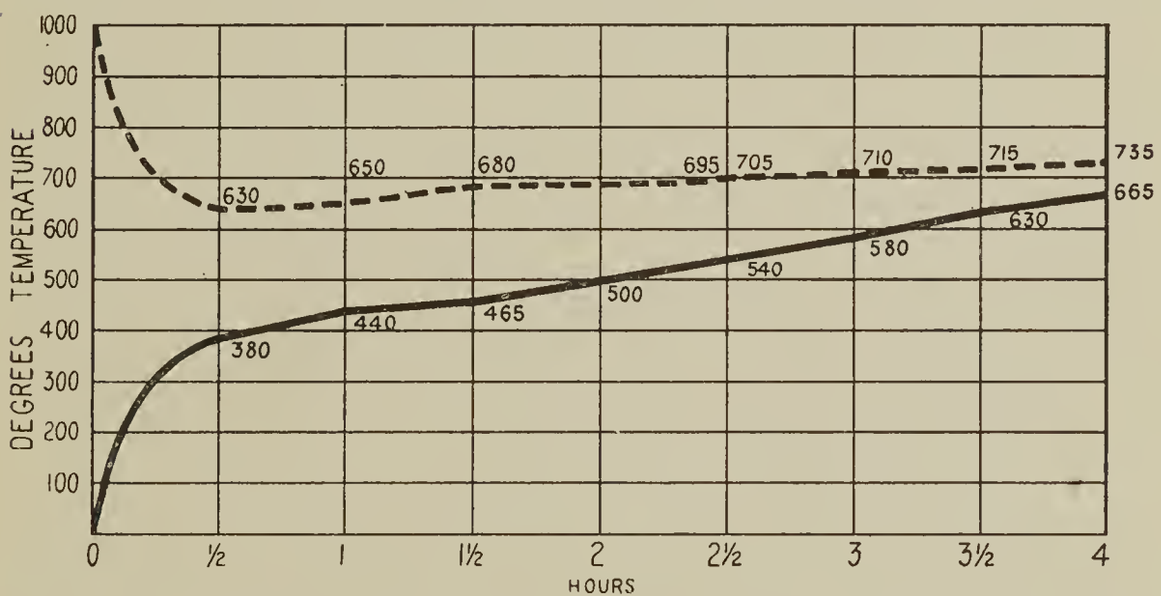


Fig. 22A.—Rise of carbonisation during carbonisation in centre of charge.

after which its rise in temperautre slows down, and it takes two hours to reach 800° C. (1472° F.). After this it heats more rapidly and attains 1000° C. (1832° F.) at the end of four hours, and then there is practically no rise in the last two hours of carbonisation. The temperature at the top of the charge rises more slowly, and by the end of the second hour is only 740° C. (1364° F.), or 60° cooler than the bottom, and remains at a lower temperature throughout the whole carbonisation. This is not to be wondered at, as although the top flue of the setting is 1150° C. (2102° F.), and the bottom flue barely 1100° C. (2012° F.), the coal at the top of the charge is being heated largely by radiant heat acting across a considerable space, whilst the bottom of the charge is in direct contact

with the heated bottom of the retort, and is taking in heat by conduction.

The thermo-couple in the centre of the charge throws most light upon the course the distillation is taking, and we discover that so great is the heating effect of the gases and vapours passing up from the hot zone at the bottom of the retort that at the end of the first hour the temperature is only 30° below that of the bottom, 730° C. (1346° F.), whilst in two hours it is at the same temperature, and then falls slightly below it for the rest of the time, the rush of hot gases from the bottom having ceased, and the temperature of the top of the charge equals the centre only after the fourth hour.

Now the fact that differences in temperature are so small throughout the mass, and that during the whole of the period when the bulk of the gas is being evolved the centre of the charge is hotter than the top, points to the gas forcing its way through the pasty mass of distilling coke upwards into the space below the crown of the retort, where it is baked by radiant heat from the mass of fireclay at 1050° C. (1922° F.), and is in surface contact with the retort walls at 1050° C. and the coke at from 700° to 1000° C. (1292° to 1832° F.).

The passage of the gas through the pasty coke causes considerable swelling during the first hours of distillation, and when the shrinkage in the charge of coke takes place during the last two hours, the upper portion, presumably carbonised by radiant heat from the top of the retort, shrinks over a smaller depth than the lower and larger portion, so that when the charge comes to be drawn, there is found to be a fissure running horizontally between the upper and lower portions but nearer to the top, from which vertical cracks branch to the top and bottom of the charge.

We are at present dealing only with the thermal conditions existing during carbonisation, but when we come to study the more chemical side of the actions taking place, we shall

see that such methods are the most brutal form of distillation —high heats and small charges certainly mean high makes of gas, but got at the expense of all the other by-products, and bringing in their train all the troubles of stopped ascension pipes, carbonised retorts, ruined tar, and poor coke. If, instead of using a 6-inch charge in such a retort, it be filled with coal as nearly as a horizontal retort can be filled, that is, to within two or three inches of the apex of the crown of the retort, and the same temperatures as before are used in the setting, we approach to the same conditions that obtain in vertical retorts, which are entirely filled, and quite different results are obtained.

The improved results are by most observers ascribed to the doing away with the baking chamber above the charge, radiant and contact heat being credited with the formation of free carbon and naphthalene, which have been the chief curses that have accompanied the raising of temperatures with small charges to increase the gas volume obtained.

The determination of temperature as before in the charge shows that filling the retort does a great deal more than this, however. In the first place, in order to properly carbonise the charge, the heating has to continue from eight to twelve hours instead of six, and the heat is poured into the charge in a much more even manner, the rise in temperature at both top and bottom being equal throughout the distillation, and with the top temperature always about 100° C. (212° F.) more than the bottom, truly reflecting the difference in temperature between the top and bottom flues of the setting. Owing to the thickness of the charge having been doubled the heat advances more slowly into the mass, rendering the coal semi-fluid and pasty in front of it, and so forming the whole centre of the charge into a tube through which a large proportion of the gas finds its way down to the mouth of the retort without having been overheated in the crown.

That this is the true explanation is shown by the thermo-

couple in the centre of the charge, which during the first 5½ hours of the distillation rises slowly in temperature at about the same rate as the outer portion, but on a plane 500° C. (932° F.) below it, whilst after this period the central heat rises rapidly, and the same temperature as exists at the bottom of the charge is attained in the eighth hour.

The gas is improved, because only a small portion has to run the gauntlet of overheating; the tar is improved, because a considerable proportion is made at a lower temperature; the coke is improved, because in the earlier half of the distillation a good deal of tar has condensed in the cool zone, and as the temperature rises the more volatile portions redistil, but the least volatile remain and get decomposed only in the last two hours of the carbonisation, which makes the coking slower, and is continued for a longer period.

It must be clearly borne in mind that the possibility of filling a horizontal retort to within three inches of the crown, although suggested by Kunath in 1885, is a comparatively new condition, which could only be achieved by the introduction of discharging machinery that would push the charge of coke out of the retort, and that as long as we were dependent upon hand labour to draw the charge, it was impossible. Now, however, the introduction of vertical settings allows a more complete filling of the retort by gravity, and easy discharge, so that the question of the route taken by the gas in its escape from the carbonising mass is receiving its full share of attention, and opinions on this subject are by no means unanimous.

Dr Bueb, to whom we owe the inception of the Dessau vertical retorts, is strongly of opinion that the largest bulk of the escaping gas finds its way through a cool core in the same way that it undoubtedly does in a well-filled horizontal retort.

It is interesting to note, however, that this was not his original idea on the subject, as in his patent, applied for in July 1902, he says, " The use of vertical retorts was tried and

even practised in the early days of gas manufacture, but was given up on account of the disadvantages it presented, one of the most serious of these being the poor quality of the gas obtained. In all such retorts the gas left the retort only at the upper part, usually through a side outlet, and the gas produced at the lower part of the retort had to pass through the whole of the column of incandescent material before it could escape, and consequently the highly valuable lighting and heating hydrocarbons first evolved were decomposed into hydrocarbons of less value, whilst a troublesome formation of graphite took place." To avoid this trouble he provides the vertical retort with ports or outlets at intervals throughout its length, so as to conduct the gas into a cool exterior duct by which it is led away.

M. Sainte-Claire Deville, however, has pointed out that during the earlier periods of distillation in a vertical retort the bottom pressure is extremely high, but decreases as carbonisation proceeds, from which he deduces the conclusion that the gas passes more easily through the coke than through the core of uncarbonised coal, and further, if the gas goes up the cool inner core, how is the heavy deposit of graphite on the walls of the retort to be explained ?

When at the end of the carbonisation steam is introduced at the bottom of the retort one of its functions is to convert this graphitic deposit into water gas, so that it must manifestly pass up the wall of the retort. Mr W. R. Herring, however, in his experiments with fully charged inclines, to a great extent corroborates Dr Bueb, in that the gas passes mostly up the cool core.

There are still some observers who favour the theory that the major portion passes up the sides, whilst Dr Harold G. Colman and many others agree that, as the pasty area of the decomposing coal works its way inwards from the walls of the retort to the centre, gas escapes on both sides of it, so that a portion goes up the centre and the remainder

through the hot coke or up the walls of the retort. What proportions exist between the gas that takes the cool route and that which is forced to pass through the hot coke cannot be exactly determined, and would vary with every kind of coal, but what we do know beyond doubt is that a large volume of the richest gas comes off from all coals when first heated, so that a large evolution of primary gas will be on the inside of the tube of semi-fused coal; whilst another factor which would tend to make the gas take the inner route is that any passing back into the hot zone would be expanded by the temperature, whilst the still pasty coke would offer more resistance to the passage of the gas than the coal, so that pressure would be highest on the hot side and lower on the cool, the probabilities therefore being that as long as the central passage is unimpeded the major portion of the gas passes up the centre. The analyses of the gas, however, all show that far too much cracking of the rich hydrocarbons has taken place.

The temperatures in the centre of the charge in a vertical retort of the Dessau pattern have been given as :—

	° C.	° F.
Wall of retort	1400	2552
Centre of charge—		
$\frac{1}{4}$ hour after charging . .	90	194
$\frac{1}{2}$,, ,, . .	105	221
1 ,, ,, . .	145	293
2 ,, ,, . .	200	392
3 ,, ,, . .	280	536
4 ,, ,, . .	370	698
5 ,, ,, . .	440	824
6 ,, ,, . .	470	878
7 ,, ,, . .	500	932
8 ,, ,, . .	580	1076
9 ,, ,, . .	620	1148
10 ,, ,, . .	950	1742

In all probability the tar-logging of the central core would become serious between the sixth and seventh hour.

It is clear that the size of the coal in the centre of the charge must have a considerable influence on the length of time that the free way for the escape of gas will remain unchoked, a large quantity of smalls proving fatal to good candle power, by choking too rapidly.

It must be remembered also that, although large coal gives the greatest clearance space, it reduces the surface of coal exposed to the heat, which is an important factor in actions such as are taking place during destructive distillation, and that to obtain the best conditions of size of coal one must consider how far the size can be reduced in order to increase the surface without too far reducing the clearance.

	Will not pass.	Will pass.	Clearance per cent. of retort space.	Surface of coal per cubic foot of coal.
Large coal .	5″ mesh	...	47	7
Medium coal .	3″ ,,	5″ mesh	46	10
Large Nuts .	$1\frac{3}{4}$″ ,,	$2\frac{1}{2}$″ ,,	44	22

Below this size clearance diminishes so rapidly that for the best results the central core should contain little if any coal smaller than "Large Nuts." This is a difficult condition to attain, as when a charge is shot from above into an empty vertical retort of the intermittent type, there is always a tendency for the charge to pack most closely in the centre of the retort throughout its whole depth and to be loosest round the sides—the exact reverse of the conditions that would give the best results—as we want the coal dense round the sides so as to conduct the heat as quickly as possible into the charge, whilst the centre should be loose with plenty of clearance to carry away the gas.

In order to attain as favourable conditions as possible with broken coal of all sizes, such as is found in the ordinary coal store, attempts have been made to devise feeding arrangements in which, whilst passing into the retort, a rough screening of the material takes place, the fine coal which passes the screen being shot to the side of the retort and the larger coal going to the centre.

I have had a considerable experience in carbonisation in vertical $5\frac{1}{2}$ to $6\frac{1}{2}$ inch tubes at all temperatures, and find that for a considerable period, although the gas escapes freely up the central core, it comes off so fast as to create a bottom pressure, but a time soon arrives with a column of this thickness in which the least volatile constituents of the tar condense in the central core, and so choke it that the pressure rises to an undue degree in the lower half of the tube, and causes serious leakage at the bottom door of the retort, whilst some gas vapours are forced from the lower half of the charge through the already choked portion and along the walls. As pressure is the most fertile source of carbon deposits in a retort, this is a serious consideration.

When we are dealing with a well-filled horizontal retort, we have an oblong mass of coal, 18 to 20 inches wide by 12 thick, and the heat advances so slowly that there is but little fear of choking from tar until the distillation is practically nearly completed. The same thing will be found with semi-chamber retorts, such as were installed by Mr Thomas Glover at Norwich. These latter consisted of oblong retorts, 3 feet high, 1 foot wide, and 21 feet long, taking 21 cwt. of coal as a charge, which required 12 hours for its proper carbonisation. In these chambers the course of the heat was manifestly inwards from the sides, which constitute the largest heating area, this being shown by the fracture of the coke on drawing being vertically down the centre.

It has been seen that with the horizontal retort the coke on drawing has a horizontal fissure or fracture through the

mass, the heat having passed into the charge chiefly from the top and bottom. The fracture in a coke charge is due to tar distilling forward before the advancing heat in the charge, and portions condensing at the coolest spot to be afterwards redistilled as the heat reaches the centre of the charge. This takes place during the last two hours of the carbonisation, during which time the remainder of the coke is

Fig. 23.—Fracture in coke in fully charged retort.

contracting and becoming denser under the prolonged action of heat, which shows itself by the charge shrinking from the walls and also from the still soft central layer, leaving the fissure in the finished coke. When the carbonisation is carried out in a tube, the fissure becomes a hole in the centre of the rod of coke, the sides of the hole showing ample signs of the carbonised tar, whilst if forced from the tube two hours before carbonisation is completed, the core is found to consist of coal and soft pitch.

In coke ovens, in which a large mass of coal is heated from the sides, the fissure (or plane of separation, as it is best called, to distinguish it from the planes of cleavage, which

as a rule are nearly at right angles to it) is vertically down the centre, when the oven has been properly heated, and the two sides are at the same temperature, but if the two sides

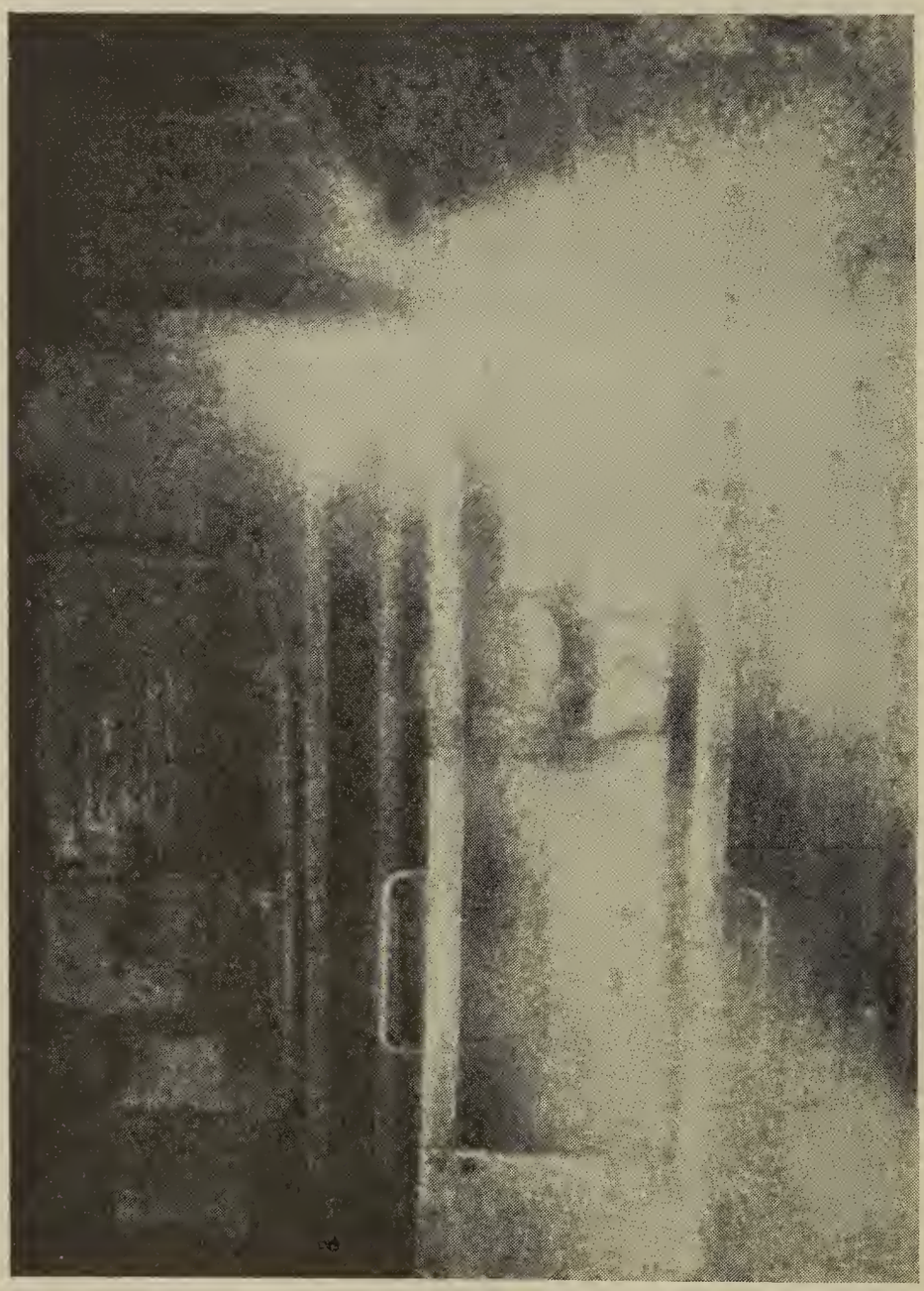


Fig. 24.—Fracture in coke-oven coke.

are not at the same temperature the plane of separation is found nearest to the cooler side.

There is a wide difference between coals of very much the same ultimate composition in the way in which they are

affected by heat during carbonisation, and the value of the coke produced will largely depend upon the conditions of carbonisation being made to fit the behaviour of the coal —a point to which sufficient attention has not yet been paid in the manufacture of coal gas. This has made itself felt in the introduction of the vertical retort, in which it is found that certain classes of coal give rise to undue swelling of the charge in the earlier stages of carbonisation, and so lead to choking of the top of the retort. When horizontals with a 9-inch space above the coal were used it did not matter how much or how little the coal swelled, but with a completely filled vertical retort it becomes a serious question.

The swelling of a coal during destructive distillation is largely dependent upon its degree of fusibility. If a coal fuses easily and the products are fairly liquid, the gases escape from it readily by the bursting of the tar bubbles formed, and the swelling is but slight. So also, infusible coals, which undergo but little softening, give no trouble in this respect, but coals which yield a tough viscid mass form large bubbles and give rise to troublesome swelling, this showing itself even more with low temperature carbonisation than with high heats. This was one of the factors that gave serious trouble in the manufacture of " coalite."

In the manufacture of coal gas in lightly charged horizontal retorts not only does the length of travel that the escaping gases have to undergo through red hot coke vary through the whole process, but the length of time they are exposed to radiant heat in the crown of the retort, and the amount of contact with the highly heated fireclay surface also vary to an extent that makes any uniformity of action or result an impossibility.

The products of distillation from the coal near the mouth of the retort, be it horizontal, vertical, or sloped, have only a short travel to reach the mouthpiece, and are hurried on by the gas behind them, so that the time given for secondary

reactions is curtailed to a fraction of a second, whilst the gas from the end of the retort has nothing to drive it forward, and has to run the gauntlet of surface action and baking to an extent that results in little else than hydrogen and carbon. Between these two limits every degree of secondary reaction is to be traced, and the gas and tar obtained are a mixture of the results of everything from low temperature distillation for a short period to high temperature distillation for a long period.

The temperature of the gas as it reaches the mouthpiece of the retort shows but little of these variations in individual portions of the gas, as they are going on pro rata throughout the whole time of carbonisation, and the thermo-couple or thermometer registers merely the mean temperature of the volume of escaping gas, so that as the period of carbonisation proceeds and the bulk of distilling gases and vapours grows smaller, the temperature of the escaping products grows less, although coming from a mass at a higher temperature.

It will be found that at the usual carbonising heats, as soon as the gas begins to escape freely, the temperature at the mouthpiece will be approximately 400° C. (752° F.), and that this will remain fairly constant until the fifth hour, whilst the falling off in volume during the fifth and sixth hours is reflected by a gradual fall in temperature of about 100° C. (212° F.). As might be expected, the slowing down of the rate of flow of gas and vapour is shown even more by the temperature at the top of the dip pipe, which rises with the first rush of gas to 120° C. (248° F.), and then steadily falls to about 50° C. (122° F.), by the end of the period of carbonisation.

The temperature of the gas escaping from the mouthpiece of an intermittent vertical retort is stated as being :—

				° C.	° F.
1 hour	after	charging	. .	190	372
2	,,	,,	. .	310	590
3	,,	,,	. .	315	599
4	,,	,,	. .	318	612·4
5	,,	,,	. .	217	422·6
6	,,	,,	. .	215	419·0
7	,,	,,	. .	213	415·4
8	,,	,,	. .	210	410·0
9	,,	,,	. .	205	401.0
10	,,	,,	. .	188	370·4

which suggests that the gas is not heated to the same extent as in the lightly charged horizontal retort.

In the secondary reactions taking place in the retort, pressure plays an important part, and as pressure is being created constantly by the evolution of gas, expansion, and decomposition, the maintenance of an even pressure is a matter of great difficulty, and where the dip-pipe and hydraulic main are used, although the retort house governor may keep the pressure steady in the hydraulic main itself, the escaping gas will be subjected to " throbs " of pressure as the gas forces out the liquid in the dip and escapes into the hydraulic main. When the gas is escaping rapidly these changes of pressure succeed each other so rapidly that the effect in the retort is a pulsation, whilst as the flow of gas slows down the individual " throbs " become more and more distinct, and short as their duration may be, they add to leakage and to decomposition.

In many works little or no attention is paid to the size of coal used, and the coal as it comes from the truck, barge, or ship goes into the retort, only the lumps so large as to give trouble being broken, and it is manifest that the flow of heat into the mass must be considerably affected. In the manufacture of furnace coke uniformity in size in the coal is looked

upon as being as important as amount of moisture and other factors of the same kind.

It is clear from these considerations that in the destructive distillation of coal for the manufacture of gas there is no one factor of uniformity in any part of the process.

It is also clear that in modern carbonisation it has been the abolition of over-heating both by contact and radiant heat in the empty space above the coal charge of practically the whole of the gas evolved that has given the improvement found with the full charges, chambers, and vertical retorts; but some time before these methods had been introduced another way of reducing the evil was suggested.

In a lecture I gave before the Incorporated Institution of Gas Engineers in 1900 I suggested that instead of using water gas merely as a diluent, it should be made a factor in the distillation itself. I then proposed that a stream of water gas should be passed through the crown of the retort during the process of carbonisation, so as not only to hurry the newly-born hydrocarbon gases out of contact with the hot walls of the retort, but also by diluting them to prevent the secondary reactions which were so important a factor in the production of tar from taking place, and by so doing to save many of the important lighting and heating constituents from destruction.

Through the kindness of Sir George Livesey and Mr S. Y. Shoubridge experiments were shortly afterwards made at the Crystal Palace District gasworks, giving results which pointed to this method of utilising water gas as of great importance. The results obtained will be further discussed when dealing with the influence of the methods employed in carbonisation on the volume, heating, and lighting power of the gas produced. It was shown, however, that it was only in the early stages of carbonisation that the use of water gas showed beneficial results. The reason for this is perfectly clear.

Messrs Folkard and Heisch showed that with six-hour charges only one-sixth of the coal remained uncarbonised at the end of the third hour. This remained as a core in the charge surrounded by a crust of three inches of coke, and as the coke would be at a temperature not very far below that of the retort, the heavy hydrocarbons evolved during the last period of the carbonisation would have been so degraded by filtering through the heated crust that the water gas would have but little chance of showing any profitable influence.

The use of water gas for this so-called " auto-carburetting " process was adopted in several German works, and in 1905 Herr Blass of Essen made some interesting experiments to see if it were possible to distil coal direct by means of superheated water gas passed through a mass of coal.

When one considers the difference that exists between the amount of heat actually required to decompose the coal, and the amount that has to be supplied in an ordinary setting, owing to the bad conducting power of retort and charge, it is clear that enormous economies could be attained by an internal process of this character.

As has been pointed out, the last three hours with a six-hour charge is needed to carbonise the inner core of partially coked coal, and although it would not be possible to obtain hard coke, still with some classes of coal a valuable fuel might be obtained by distilling the coal in a stream of red-hot water gas, and absolute control of temperature could be obtained.

As we have seen, the coals constituting the class of gas and coking coal are probably slightly endothermic ; indeed, some theorists have considered the heating of coal during weathering as being due to their endothermicity, and have claimed that some coals could be coked by the heat they themselves developed during this action. My own experience, however, is opposed to this, as with the coals I have experimented with,

weathering is an action which continues for a few months and then practically ceases, owing to the resinic constituents, which by their affinity for oxygen set up the action, becoming converted into humus bodies or other more highly oxygenated compounds, so that when a mass of coal in a store fires or cokes it is the heat of slow combustion that is the cause.

Blass used a metal retort jacketed by a bath of molten zinc, through which passed a worm tube to heat up the gas passed into the coal to be distilled. Using ·66 lb. of coal, 22·4 cubic feet of water gas were passed through the apparatus with the zinc bath at a temperature of 672° C. (1242° F.), the experiment being stopped when the gas became non-luminous. The results were ·447 lb. of coke, 68 per cent., but the amount of water gas was far too high and the temperature too low. The experiment showed, however, that the yield of ammonia was largely increased.

In this form the experiment was of little or no use, but the idea of getting away from the troubles due to the low conductivity of the retort and material is one that is well worth further consideration, and although the mechanical side of the question would present very great difficulties, it is quite probable that when the heating value of a gas admittedly becomes of paramount importance, and mixtures of water gas with just enough hydrocarbons to bring them up to the useful heating limit become the aim of the gas manager, some process based on these principles may become of great value.

CHAPTER VI

THE PRIMARY GASEOUS PRODUCTS OF THE DESTRUCTIVE DISTILLATION OF COAL AND THE BODIES FROM WHICH IT HAS BEEN FORMED

The distillation of wood at low temperatures—Composition of the gases evolved—The gases given by wood at high temperatures—Peat—Composition of peat and its destructive distillation—Lignites and their composition—The work of Ste Clair Deville—Analysis of the coals used and the results obtained—Constam and Kolbe's experiments on coals—Reason for the differences found—Euchêne's results—Effect of oxygen in coal on the products of distillation—Composition of humus and resin bodies—Discussion on Constam and Kolbe's work—The experiments of Lewis T. Wright—Coalite—Low temperature carbonisation—The researches of Porter and Ovitz on low temperature carbonisation—The work of White, Park and Dunkesley on American coals—Messrs Burgess and Wheeler's experiments—Primary and secondary reactions.

THE gases evolved by coal during the process of carbonisation depend upon two factors :—

1. The composition of the coal distilled.
2. The temperature employed, which influences the composition by governing the amount and character of the secondary reactions taking place.

Of the four classes of bodies which in their agglomeration yield coal, the carbon residuum is the only one which does not decompose under the influence of heat, and the humus, resin, and hydrocarbon bodies are the portions of the coal that condition its gas-yielding properties.

Our knowledge of the hydrocarbons formed from the resin bodies is not sufficient to allow any successful attempt to

discriminate between the kind and quantity of the gas yielded by them and by the hydrocarbons formed from them, so that we may look upon the hydrocarbons as included in the general term "resin bodies."

We have seen that the humus and resin bodies each yield distinctive products of decomposition, and a great deal may be learnt by studying the differences in the gaseous products of the destructive distillation of the substances which represent the stages in the formation of coal, whilst if the products formed at the lowest temperature of distillation be ascertained, we can form a fairly accurate idea of the primary products of decomposition and the secondary reactions taking place at higher temperatures.

In 1892 some very valuable researches were made by Chorley and Ramsay upon the destructive distillation of wood. They heated the wood (oak, beech or alder) in a flask by means of an air bath, in which the temperature could be kept constant by triple walls, the temperature in both flask and air bath being recorded by nitrogen thermometers. The flask was connected to a condenser, washing and absorbing bulbs, and the residual gas was then collected. The whole of the apparatus was as far as possible exhausted by a water pump before commencing the distillation, and the material in the flask, which was in the form of fine chips, was heated at between 330° and 400° C. (572° and 752° F.), until all gas ceased to come off. Under these conditions the gases evolved were as follows :—

	Oak.	Beech.	Alder.
Carbon monoxide .	86·7	83·4	78·3
Carbon dioxide . .	6·4	6·2	7·4
Methane . . .	2·7	3·3	4·0
Nitrogen (by diff.) .	4·2	4·9	8·8
Oxygen . . .	*nil.*	1·2	1·5

That is to say, that at this low temperature the gas evolved was for all practical purposes impure carbon monoxide.

On now raising the temperature of distillation to about 500° C. (932° F.) the result was to increase the methane to an average of about 18 per cent., with slight increase in carbon dioxide and decrease of the carbon monoxide, traces of ethylene also making their appearance.

The great interest of these low-temperature distillations is that they show that the oxygen in the wood is in such combination that carbon monoxide is the primary product of its decomposition, and that the hydrogen and carbon dioxide, which are found in wood gas made at from 800° to 1000° C. (1472° to 1832° F.), are due to the oxidation of carbon monoxide by steam with liberation of hydrogen, and also to the action of steam on the red-hot carbon.

There must have been plenty of steam present in these experiments, as the samples of wood used, after drying in vacuo for a month, still contained—

Oak, 13·58 per cent. ; Beech, 11·6 per cent. ; Alder, 11·64 per cent.

When wood is distilled at comparatively low temperatures on a large scale for tar, wood spirit, and acetic acid, the gases given off approximate mostly to :—

Carbon dioxide . .	40·0
Carbon monoxide .	36·0
Methane . . .	18·0
Ethylene . . .	1·0
Nitrogen . . .	5·0

The temperature being 400 to 500° C. (752° to 932° F.) and the high carbon dioxide being at any rate partly due to air leakage oxidising the monoxide.

The fact of increase on methane and carbon dioxide without any formation of hydrogen in Chorley and Ramsay's experiments led them to suggest that it might be due to the action of nascent carbon on water, partly present as such and partly in course of formation, according to the equation—

$$2C + 2\,H_2O = CH_4 + CO_2$$

but they admit that no trace of such reaction is to be found when steam is passed through red-hot charcoal. This, however, may be entirely a question of temperature, as at the bright red heat of a water gas generator the methane and carbon dioxide would be both decomposed, and a trace of methane is nearly always to be found in the gas.

Another interesting fact revealed by this investigation was that during the distillation of wood at low temperature, a point was always reached when, the water having all distilled off, the reaction became exothermic, that is, the temperature of the distilling wood suddenly rose above the temperature of the heated vessel, and an increase in the rapidity with which the gas was evolved took place. This rise in temperature is explained by the fact that the acetic acid, methyl alcohol, and oxides of carbon and water, which are the products of the decomposition, are all exothermic compounds that generate heat during their formation.

In none of the cases discussed has the temperature of the distillation been above 500° C. (932° F.) and when wood is distilled at about 900° C. (1652° F.) for the production of lighting and heating gas, hydrogen makes its appearance in quantity, and the composition would approximate to—

	Per Cent.
Hydrogen . .	20
Carbon monoxide .	30
Carbon dioxide . .	27
Methane . . .	18
Ethylene . . .	2
Nitrogen . . .	3

Messrs Chorley and Ramsay at a later date used the same methods and apparatus to investigate the action of heat upon jute and cotton wool, bodies which we have seen may be taken as representing jute the lignose, and cotton the cellulose, in the growing plant.

They found that when distilled at temperatures between

300 and 400° C. (572° and 752° F.) the jute fibre gave practically the same volume of carbon monoxide as the wood, but that the purified cellulose gave only about 50 per cent. They unfortunately did not analyse the gas for methane and hydrogen, so that it is doubtful of what the residual gas consisted.

One of the most comprehensive researches with regard to the effect of the composition of the fuel carbonized on the products is that made by Dr Bornstein in 1906. He not only distilled wood, peat, lignite, and coal and contrasted their products, but also did it at temperatures varying from the lowest temperature at which decomposition occurred up to 540° C. (842° F.), so as to cover the whole of the little known changes taking place below those of ordinary distillation.

Wood—dried deal. Composition :—

Carbon	48·75
Hydrogen	6·48
Oxygen	40·75
Nitrogen	0·63
Sulphur	0·08
Ash	0·10
Moisture	3·21

The gases evolved were as follows :—

	300-350° C. 572-662° F.	350-400° C. 662-752° F.	400-450° C. 752-842° F.
Carbon dioxide	53·5	55·0	28·0
Unsaturated hydrocarbons	0·2	1·5	5·0
Methane	14·9	7·9	20·6
Carbon monoxide	27·7	32·6	29·0
Hydrogen	3·7	3·0	17·3

The first gas (carbon dioxide) appeared at 165° C. (329° F.), water at 180° F. (356° C.), inflammable gas at 280° C. (536° F.), tar at 300° C. (572° F.).

It is clear from these two sets of experiments that the

woody fibre, the substance from which all the humus bodies have sprung, commences to decompose at about 200° C. (392° F.), and that water and carbon oxides are the primary products ; and it seems probable from Chorley and Ramsay's experiments that it is the monoxide which is first produced, they having taken the precaution to remove the air from the distillation flask. Methane is the next gas to make its appearance as the cellulose structure undergoes destruction ; but it is also a primary product, and then as the temperature rises other hydrocarbons and the tar bodies appear, whilst secondary reactions make hydrogen an important constituent of the gas.

It is interesting to note that the three primary products of destructive distillation—water, oxides of carbon, and methane—are the same as the products of checked decay and the gases which we find occluded in our coal measures.

The fact that peat is intermediate in composition between the celluloses and lignites has led to the adoption of the idea that it represents the change of state that wood undergoes in its conversion into lignite, and it is so stated in every text-book—I have made the statement so often that I ought to believe it—but the more I see of peat bogs and peat the more I feel convinced that although peat may represent a condition of vegetable decay falling between the stages of vegetable matter and tertiary coal, it does not represent the change in ordinary vegetable matter, but in the British Isles at any rate is mostly, if not all, composed of the remains of sphagnum or peat moss, which, growing from above and decaying from below, builds up the deposits we know as peat bogs.

Whether you examine the peat bogs of the eastern counties, of Dartmoor, of Scotland, or of Ireland, you find the same characteristics. If the bog has not been buried by soil, there is the growing sphagnum on top, building up the deposit

at a rate that can be measured by inches in years ; there is the light peat of the upper portion of the bog, gradually darkening as you dig down into the water-logged mass until you reach the rich black peat in the lower part of the deposit ; whilst the antiseptic properties of the humus, which has mummified and preserved human and animal remains for centuries, and which has protected the stems and roots of trees from decay, does not by any means suggest changes that would convert ordinary vegetation into coal, although fully explaining the resistant properties of peat to decay, so allowing the accumulation of the vast deposits existing on the surface of the globe. Under other conditions, such as those existing in the carboniferous age, which led to any deposits being deeply covered with silt and sand, the action of long ages of heat and pressure might well convert peat into coal, but not ordinary vegetation, such as we know to-day, into peat.

In other countries, however, peat bogs of a totally different character exist, built up from all kinds of vegetable deposits. Peat varies as widely in composition as the great class of tertiary coals, and unless one knows the ultimate composition of a sample of peat as well as its proximate analysis, the results of its destructive distillation afford but little information as to the course the decomposition is taking.

Bornstein in his experiments in the low temperature distillation of peat obtained the following results :—

Peat

Composition of ash- and moisture-free peat.

Carbon	58·5
Hydrogen	5·5
Oxygen	32·7
Nitrogen	3·0
Sulphur	0·3

The gases evolved were as follows :—

	300-350° C. 572-662° F.	350-400° C. 662-752° F.	400-450° C. 752-842° F.
Carbon dioxide . .	89·2	63·8	55·4
Carbon monoxide . .	10·1	7·2	12·3
Unsaturated hydrocarbons	0·3	0·4	3·7
Methane	*nil.*	25·5	25·4
Hydrogen . . .	0·3	3·1	3·1

Water appeared at 100° C. (212° F.), gas at 250° C. (482° F.) (carbon dioxide), tar at 325° C. (617° F.), and inflammable gas at 400° C. (752° F.).

Euchêne, whose work I have already quoted, made an analysis of peat, and distilled it under gasworks conditions, with the following result :—

	Peat as used.	Ash and Water-Free.
Carbon . . .	47·475	62·073
Hydrogen . . .	5·207	6·807
Oxygen . . .	22·975	30·040
Nitrogen . . .	0·825	1·080
Sulphur . . .	0·676	..
Ash	5·342	..
Moisture . . .	17·500	..
	100·000	

Volatile Matter . .	71·050	Composition of the tar.	
Gas . . 36·250		Carbon . .	86
Tar . . 8·300	71·050	Hydrogen .	6
Water . 26·500		Oxygen . .	8

Gas yield . . 15,000 cubic feet per ton.

Composition of the gas :—

Hydrogen	30·76
Methane	27·60
Ethylene	7·40
Benzene	1·20
Carbon monoxide	22·25
Carbon dioxide	9·46
Nitrogen	1·33

In considering these analyses it must be noted that the peat used by Bornstein was of a fair average composition with the exception of its richness in nitrogen, whilst that used by Euchêne must have been a rich old peat in which already concentration of carbon and hydrogen and elimination of oxygen had given it more the composition of a lignite, which accounts for the richness of the gas in unsaturated hydrocarbons.

Analysis I have made of peat gas from time to time average :—

Hydrogen	31
Methane	26
Ethylene	3
Carbon monoxide	23
Carbon dioxide	12
Nitrogen	5

and it is clear that the decompositions taking place in the peat structure are identical with those found in the case of wood.

Passing to the next link in the chain between vegetation and coal, we come to the experiments made by Bornstein on the low temperature products of the distillation of lignites of two different ages of formation :—

LIGNITE

	I. Recent Herzhom.	II. Old Bohemian.
Carbon	55·1	69·5
Hydrogen	·42	5·5
Oxygen	36·5	23·6
Nitrogen	0·9	1·0
Sulphur	3·4	·04

I

Gas evolved—	350-400° C. 662-752° F.	400-450° C. 752-842° F.	440-450° C. 752-842° F.
Carbon dioxide	56·7	52·1	42·6
Carbon monoxide	10·9	20·0	8·1
Unsaturated hydrocarbons	1·6	1·5	4·0
Methane	18·9	18·1	8·0
Hydrogen	11·9	7·4	19·3
Ethane	*nil.*	0·9	18·0

II

	300° C. 572° F.	350° C. 662° F.	400° C. 752° F.	450° C. 842° F.
Carbon dioxide	92·7	91·0	55·1	27·7
Carbon monoxide	1·2	4·7	18·9	11·6
Unsaturated hydrocarbons	0·1	0·2	4·9	2·4
Methane	5·5	3·4	16·0	38·6
Hydrogen	0·5	0·6	2·2	15·0
Ethane	..	..	2·9	4·7

I. Water appeared at 100° C. (212° F.), gas at 210° C. (410° F.) tar at 350° C. (662° F.).

The lignites, which form the great tertiary class of coals, are not often distilled for gas, as the high percentage of oxygen they contain leads to the formation of a high percentage of oxides of carbon, and as a considerable proportion of this is

present as the dioxide, purification by lime would become a heavy item. The volume of gas they give, however, is large.

The following details of the distillation of a lignite at gas-making temperatures are due to Dr E. J. Constam, of Zurich, and the material used was the French Gardanne lignite :—

Composition of the Lignite

Lignite.		Combustible Matter.		Yields.	
Moisture .	10·55	Carbon . .	73·31	Coke .	50·6
Ash .	10·79	Hydrogen .	5·06	Volatile .	49·4
Combustible	78·66	Oxygen .	14·00		
		Nitrogen .	1·63		
		Sulphur .	6·00		

	Gross.	Net.
Calorific value of Combustible	12·981	12·346

Yield of Products per cent.

Coke	50·60	
Gas	25·60	= 12,619 cub. ft. per
Tar	4·55	ton ; sp. gr. 0·595 ;
Pitch	2·00	B.Th.U. 512 gross.
Liquor	16·45	

Composition of the Gas

Hydrogen . .	42·53	Carbon dioxide	9·47
Methane . .	20·70	Oxygen .	0·28
Ethylene . .	4·75	Nitrogen .	3·85
Carbon monoxide .	18·42		

Here, again, the diminution of oxygen in the original material as compared with wood and peat is marked by a fall in the quantity of oxides of carbon in the gas.

The facts that stand over clearly from these experiments

upon the highly oxygenated fuels, and also from the earlier experiments upon them that I have quoted, are that on heating bodies like wood and bodies which are rich in humus compounds, like peat and lignite, the low temperature decomposition is the formation of water and oxides of carbon, the latter forming practically the whole of the gaseous products below 350° C. (662° F.), whilst between 300° and 400° C. (572° and 752° F.) any resin bodies that are present in the peat or lignite begin to decompose, and hydrocarbons and tar make their appearance. It is also to be noted that as soon as the vegetable matter has reached the condition of change in which some of the resin bodies are in the form of hydrocarbons, saturated hydrocarbons richer than methane make their appearance, and even denser members of the paraffin series.

Dr Bornstein next distilled samples of eight kinds of coal. The results are given in the large table, but I have placed them in the order of oxygen content in the coal substance, because I want to bring out the following point. All the coals distilled at this temperature yield considerable quantities of ethane and unsaturated hydrocarbons. If these were due to the humus bodies they would increase with excess of oxygen in the coal substance, whilst if they were due to resin, they would increase with decrease in the oxygen; but as they are yielded in each case and their quantity bears no relation to the oxygen, it is a fair inference that they are formed by the hydrocarbons which are derived from the resin bodies.

In the early years of the gas industry the use of iron retorts necessitated the employment of temperatures which were low as compared with those to which we are accustomed to-day, but were still well above the point at which secondary reactions in both the gaseous and vapourous constituents of destructive distillation were taking place, and in all probability the true low temperature distillation of coal, that is,

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Composition of ash- and moisture-free coal :—								
Carbon . . .	80·99	82·87	84·90	85·09	86·04	86·70	88·02	89·25
Hydrogen . . .	4·67	5·06	4·44	4·82	5·18	5·35	5·20	4·46
Oxygen . . .	12·26	9·64	8·13	7·95	6·25	5·58	4·79	3·06
Nitrogen . . .	1·13	0·70	0·98	1·08	0·88	0·81	0·93	0·95
Sulphur . . .	0·95	1·73	1·55	1·06	1·65	1·56	1·06	2·28
Gaseous products, 450° C—								
Carbon dioxide . .	16·1	6·0	6·6	3·8	5·3	5·5	15·5	18·5
Carbon monoxide .	8·8	5·0	5·4	3·8	6·2	2·5	1·8	2·4
Unsaturated hydrocarbons . . .	13·0	9·7	14·3	5·6	10·0	10·3	8·5	5·9
Methane . . .	38·4	47·8	39·4	54·3	44·2	71·5	40·1	60·1[1]
Ethane . . .	17·2	24·1[1]	28·2[1]	15·2	28·3		21·3	
Hydrogen . . .	6·5	7·4	6·1	17·3	6·0	10·2	12·8	13·1

Water first began to appear at about 200° C. (392° F.) in each case. True distillation began between 300 and 400° C. (572 and 753° F.).

[1] These contained also higher saturated hydrocarbons.

at temperatures when little else than primary products of the decomposition were being evolved, would never have been attempted on a manufacturing scale, had it not been for the attempt in 1907 to introduce the low temperature coke known as " coalite " as a smokeless fuel. I made a number of experiments on the subject, and in a course of Cantor Lectures in March 1908, whilst describing the process, gave the following figures.

" When an ordinary gas coal is subjected to destructive distillation, the volume of the gas, its heating and illuminating value, and also the quantity and quality of the tar undergo great changes, according to the temperature at which the distillation is carried out. The following table shows the average results that are obtained with a good sample of gas coal. The term " average result " is used, as variation in the coal employed introduced alterations in the results, although they will all follow similar lines.

YIELD OF GAS AND TAR PER TON OF COAL CARBONISED

Temperature of Distillation.		Volume of Gas.	Tar	Specific Gravity
° C.	° F.	cub. ft.	Gallons.	of Tar.
900	1652	11,000	9	1·200
800	1472	10,000	12	1·170
700	1292	9,000	15	1·140
600	1112	7,750	18	1·115
500	932	6,400	21	1·087
400	752	5,000	23	1·060

The following table as to the composition of the gas was also given :—

EFFECT OF TEMPERATURE OF CARBONISATION ON THE PERCENTAGE PROPORTIONS OF THE CHIEF CONSTITUENTS OF THE GAS

Temperature.	400° C. 752° F.	500° C. 932° F.	600° C. 1112° F.	700° C. 1292° F.	800° C. 1472° F.	900° C. 1652° F.
Hydrogen .	21·2	28·3	33·8	41·6	48·2	54·5
Saturated hydrocarbons .	60·1	56·2	50·7	45·0	39·1	34·2
Unsaturated hydrocarbons .	6·3	5·8	5·0	4·4	3·8	3·5

Although only 5000 cubic feet of gas are obtained from the coal, it is over 20 candle-power, and has a calorific value of 750 B.Th.U. per cubic foot, whilst the low temperature of carbonisation has reduced the sulphur compounds other than sulphuretted hydrogen to a point that would satisfy the most ardent stickler for purity.

After this date, plants were erected on a large scale for the manufacture of the low temperature coke, and I had the opportunity of studying the carbonisation of many thousand tons of various kinds of coal at the temperatures which were found to be the lowest compatible with the development of a fair amount of gas and the production of a coke still containing 10 to 14 per cent. of volatile matter, which would burn with an absolutely smokeless flame and give easy ignition with plenty of flame.

Under these conditions a fair gas coal, containing 30 to 33 per cent. of volatile matter, will yield 68 to 70 per cent. of low temperature coke, containing 10 to 14 per cent. of volatile matter, and a volume of gas varying from 3000 to 5000 cubic feet, according to the coal used, having a composition approximating to :—

Hydrogen		27·5
Saturated hydrocarbons—		
Methane	48	
Higher members . . .	10·1	
	——	58·1
Unsaturated hydrocarbons . . .		3·0
Carbon monoxide		7·3
Carbon dioxide		2·5
Nitrogen		1·6

The gas before iron purification contains about 1·8 per cent. of sulphuretted hydrogen.

The low temperature gas, of course, varies with the coal used. The hydrogen is often below 18 per cent., and the saturated hydrocarbons up to 68 per cent.; but the marked feature of the gas is that it contains hardly any benzene vapour, and owes its illuminating power to a small percentage of ethylene, and chiefly to the gaseous members of the paraffin series (mostly ethane), and also that the percentage of hydrogen is low, very rarely reaching the amount present in the above sample, whilst bisulphide of carbon likewise is very low.

The prominence given to the manufacture of coalite attracted a good deal of attention in the United States, and two very valuable researches on the distillation of coal at low temperatures were published late in 1908, the one by Messrs Porter and Ovitz, and the second by Messrs White, Park, and Dunkerley.

The work of Porter and Ovitz was reprinted by permission of the Chief of the Staff of the United States Geological Survey, where it had formed part of the fuel investigations conducted during the years 1907-08, on the nature of the volatile matter of coal as evolved under different conditions. The primary objects were (1) to throw light on the nature of the volatile products from coal and the manner in which

they are affected by the conditions prevailing during their formation, or to which they are subjected after formation; (2) to contribute in the interests of smoke abatement some data on the comparative amount and character of the gases and vapours distilled from different coals at low temperatures, a subject intimately concerned with the production of smoke; (3) to prove experimentally that the volatile products of coal are to some extent incombustible, and that the production of inert volatile matter varies in different coals; and (4) finally, to show that the oxygen of coal is in many cases evolved in the volatile matter very largely in combination with carbon as oxides, as well as with hydrogen as water, thereby explaining to a great degree the discrepancies found in these cases between the determined calorific value and that calculated by Dulong's formula.

Their first experiments were directed to noting the accumulation of combustible gas in tightly sealed jars containing samples of freshly mined coal, which were kept for ten months, and the gases then collected and analysed. They found that under these conditions the gas liberated consisted almost entirely of methane, with a very slight amount of carbon dioxide. They then determined the volatile matter from coal at 105° C. (221° F.), the temperature usually employed for drying coal during analysis, and they found that besides moisture there was a slight amount of carbon dioxide produced with only small traces of hydrocarbons and carbon monoxide, whilst the coal will often gain in weight through oxidation.

Having completed this preliminary work, they studied the nature of the volatile matter given off by the same coals at 500° C. and 1100° C. (932° and 2012° F.) in the case of four typical American coals, the tests being made upon 10 grams and 400 grams of coal respectively.

From these results they find that the low temperature gases are high in illuminants and the higher members of the

paraffin series, and low in hydrogen, and they also conclude that in the process of breaking down under the influence of heat, the coal substance gives up its oxygen partly in the form of water, and partly in the form of oxides of carbon, and point out that no calculation of calorific value from any formula which assumes that all the oxygen combines with hydrogen can be correct.

Unfortunately, they give only proximate and not ultimate analyses of all the coals used, so that the influence of the coal constituents cannot be traced, the Illinois and Wyoming coals, of which they give ultimate analyses for the purposes of their heat calculations, not being amongst those subjected to experimental destructive distillation.

Messrs White, Park, and Dunkerley made experiments on heating five American bituminous coals of widely different classes to a temperature of 300° to 500° C. (572° to 932° F.), and they confirm the high ethane content and low hydrogen found in low temperature carbonisation. In commenting upon it they make the following interesting remark : " The ethane of natural gas has been assumed to have been formed by the direct addition of hydrogen and ethylene. We have here, however, ethane forming apparently as a primary product in a gas containing only small amounts of hydrogen and unsaturated hydrocarbons, which would favour the theory that the ethane in the natural gas is also a primary product."

These observers distilled samples of non-coking, feebly coking, and good coking coals, but here again give only the ultimate analysis for one coal—the non-coking Zeigler, which contains 16·29 per cent. of oxygen, whilst one knows that the coking coals like the Pittsburg and Bay City coals will contain a far lower quantity. I will quote the composition of the gas obtained from these three coals in heating for six to eight hours at a temperature rising from 300° to 450° or 500° C. (572° to 932° F.), as the proportion of ethane

present is far higher in the one from Pittsburg coal, than in any other analysis I have seen.

	Zeigler.	Bay City.	Pittsburg.
Carbon dioxide . . .	13·1	16·2	2·9
Carbon monoxide . .	5·8	5·0	6·2
Unsaturated hydrocarbons .	1·6	4·1	2·2
Methane	38·0	37·8	26·3
Ethane	19·5	11·8	47·0
Hydrogen	13·9	16·4	13·2
Nitrogen	7·8	9·1	2·7

We now come to the latest piece of work that has been done on this subject, and which was published in the *Journal of the Chemical Society* in 1910 and 1911 by Messrs Burgess and Wheeler, and which has been referred to before. These investigators have been employed for some years on the experiments conducted by the Mining Association of Great Britain, in order to elucidate the phenomena occurring during coal dust explosions in mines. The special experiments that form the basis of their two communications were made with the view of determining the nature of the volatile constituents of coal dust, as it has a most important bearing on the problem of such explosions, and also is of great general interest from many points of view.

The coal dust experimented with had the following composition :—

	I. Bituminous. Altoft's Silkstone Seam.	II. Bituminous. Abertillery, South Wales.	III. Semi-Bituminous. Penchyegger, S. Wales.	IV. Anthracite. South Wales.
Carbon . .	80·50	85·72	90·72	92·66
Hydrogen .	5·45	4·93	4·23	3·14
Oxygen . .	9·70	7·34	1·25	2·20
Nitrogen . .	1·42	1·09	2·99	0·99
Sulphur . .	2·93	0·92	0·81	1·01

From their results they confirm the previous observers in the high percentage of methane and ethane in the gases evolved at low temperatures, and draw attention to the fact that all the data obtained by them indicate that there is a critical period in the decomposition of the coal between 700° and 800° C. (1292° to 1512° F.), the rate of evolution of gas and the total quantity evolved per gram being nearly double at 800° C. to what they are at 700° C.

The most interesting part of this research was that the authors tried the effect of distilling coals, I, III, and IV, in a vacuum maintained by an automatic Sprengel mercury pump, the heating at each temperature being kept constant in an electric resistance tube furnace for twenty-four hours in order to completely withdraw all the gas evolved at that particular temperature, before the temperature was raised another 50° C. (122° F.).

Under these conditions the amounts of hydrogen and saturated hydrocarbons evolved at the various temperatures are of great interest, and may be tabulated as follows :—

Gas evolved . . .		Hydrogen.			Saturated Hydrocarbons.		
Type of Coal . .		I.	III.	IV.	I.	III.	IV.
		cc.	cc.	cc.	cc.	cc.	cc.
Limiting Temperature	15°–350° C. 59°–662° F.	0·15	0·08	0·09	1·35	0·06	0·00
	400° C. 752° F.	2·40	...	0·11	9·85	...	0.23
	450° C. 842° F.	12·65	12·1	...	26·95	16·6	...
	500° C. 932° F.	24·10	...	5·7	25·10	...	5·92
	550° C. 1012° F.	47·00	129·2	...	19·05	42·0	...
	600° C. 1112° F.	68·65	89·2	82·6	14·50	9·95	19·70
	650° C. 1402° F.	80·60	162·2	...	8·40	5·0	...

It will be seen that up to the highest temperature employed, with the bituminous coal, the hydrogen has steadily increased in quantity, whilst the saturated hydrocarbons, after reaching a maximum at 450° C., slowly fall off as the temperature rises, a result which is not borne out by practical working on a large scale, and which I think is due to the fact that Messrs Burgess and Wheeler were using a charge of only two grams

of coal dust mixed with three grams of ignited sand, with the result that all the tar vapours formed escaped at once from the zone of heat instead of the heavier portions remaining as pitch in the residue, as they undoubtedly do in practical working, which shows that most of the methane formed in the destructive distillation of coal at temperatures above 600° C. is due to secondary reactions taking place as the pitch is carbonised.

The evidence that one can collect as to the products of the various coal constituents points to their primary decompositions as being :—

Carbon Residuum. Unaffected by destructive distillation.

	Solid.	Gaseous.	Liquid.
Humus bodies.	Carbon.	Carbon oxides.	Water.
		Methane.	Thin tar.
Resin bodies.	Carbon and pitch.	Carbon oxides.	Water.
		Ethylene.	Rich tar.
		Other unsaturated hydrocarbons.	
Hydrocarbons.	Carbon and pitch.	Ethane.	Heavy tar.
		Higher members of the series.	
		Methane.	

Hydrogen, which is the chief gaseous constituent found in high temperature gas, is not a primary constituent of the carbonisation, and the amount found in gas distilled between 400° and 500° C. (752° and 932° F.), is due to secondary reactions having already started.

Methane, which is next in importance to hydrogen in the high temperature gas, is a product of both primary and secondary reactions, and being the most stable of the gaseous hydrocarbons undergoes destruction only at high tempera-

tures, so that for the methane to fall below 30 per cent. in a coal gas made from a good gas coal means degradation of the products by overheating.

By secondary reactions we mean the action of heat upon compounds which have already been formed primarily at the lower temperature, and if one heats a coal to, say, 450° C. (842° F.) and then makes an ultimate analysis of the carbon and hydrogen which it still contains, one gains an idea of the amount of the three elements which have been driven from it by heating up to that temperature. One generally finds that the amount of hydrogen and oxygen left in will be, to a certain extent, in the same ratio as in the original coal ; that is to say, if you took a Staffordshire coal, in which the proportion of hydrogen is 5 per cent. and the oxygen 10 per cent., distil it at 450° C. (842° F.) and analyse the coke, the oxygen will be found still in a higher percentage than the hydrogen. This does not mean that the humus body in such a coal remains undecomposed whilst the resin bodies have been driven out. It means merely that the products of decomposition and residues still remaining in the mass contain compounds richer in oxygen than hydrogen. Where one has a coal, which in the first place shows an excess of hydrogen over oxygen, an excess will be found still in most cases in the residual low temperature coke. The bodies left, however, are undoubtedly different from those originally present, and under the influence of heat, when the distillation is pushed to a finish, the gases evolved are closely akin in all cases, and consist of hydrogen, oxides of carbon (in which carbon monoxide preponderates), and methane.

The effect of the temperature of distillation upon the coke and tar will be discussed fully in the chapters devoted to these products, but it must clearly be borne in mind that the low temperature gas gives only from one-third to one-half the volume of the high temperature gas obtained under

ordinary processes of carbonisation, and that the extra volume is produced partly by a degradation of hydrocarbons in the primary gas, but chiefly to the breaking up of compounds present in the tar and pitch.

In the case of wood, peat, and lignite, we studied the composition of the high temperature products immediately after the low, but in the case of the true coal we have, so far, reviewed only the researches that have dealt with distillation at temperatures likely to yield primary products, and we must now trace the effect that rise of temperature as well as composition of the coal have upon the gaseous products at heats up to those employed in ordinary gasworks' practice.

In the last half of the last century, before the incandescent mantle had made high candle-power in the gas perfectly unnecessary, a very large proportion of the work done in experiments in coal distillation and coal gas was with the object of obtaining high illuminating power, and this is largely governed by the temperature. As the temperature is raised, the yield of gas from a given weight of coal increases, but with the increase in volume there is a marked decrease in the illuminating value of the gas evolved. Mr Lewis T. Wright found, in a series of experiments, that when four portions of the same coal were distilled at temperatures ranging from a dull red heat to the highest temperature attainable in an iron retort, he obtained the following results as to yield and illuminating power :—

Temperature.	Cubic Feet of Gas per Ton.	Illuminating. Power.	Total Candles per Ton.
1. Dull red . . .	8,250	20·5	33,950
2. Hotter . . .	9,693	17·8	34,510
3. Hotter . . .	10,821	16·7	36,140
4. Bright orange . .	12,006	15·6	37,460

Composition of the Gas

	1.	2.	4.
Hydrogen . . .	38·09	43·77	48·02
Methane . . .	42·72	34·50	30·70
Olefines . . .	7·55	5·83	4·51
Carbon monoxide .	8·72	12·50	13·96
Nitrogen . . .	2·92	3·40	2·81
	100·00	100·00	100·00

The gas analysis of No 3 was lost, but the illuminating power shows that it was intermediate in composition between No 2 and No. 4. From this it will be seen that with the increase of temperature the hydrocarbons—the olefines and methane series—gradually break up, depositing carbon in the crown of the retort and liberating hydrogen, the percentage of which steadily increases with the rise of temperature.

The most comprehensive and the largest scale experiments ever made on the influence of the composition of the coal on the gas produced from it under gasworks conditions were those carried out by Sainte-Claire Deville at the experimental works at La Villette, belonging to the Paris Gas Company, extending over the years 1872 to 1884, during which time 1012 tests were made with fifty-nine different coals, each test representing the carbonisation of 35·5 tons of coal.

The coals were arranged in five classes according to their oxygen content as follows :—

	1.	2.	3.	4.	5.
Oxygen . . .	5·56	6·66	7·71	10·10	11·70
Hydrogen . . .	5·06	5·37	5·40	5·53	5·64
Carbon . . .	88·38	86·97	85·89	83·37	81·66
Nitrogen . . .	1·00	1·00	1·00	1·00	1·00
Water . . .	2·17	2·70	3·31	4·34	6·17

Whilst their proximate analysis gave :—

Volatile matter . .	26·82	31·59	33·80	37·34	39·27
Coke	73·18	68·41	66·20	62·66	60·73
Ash	9·04	7·06	7·21	8·18	10·73

Each coal was distilled alone in four-hour charges for a period of three days in two settings of seven retorts, the proportions of the different products yielded being :—

Yield per 100 kilos. of Coal

Gas, cu. metres . .	30·13	31·01	30·64	29·72	27·44
Coke, hect. . . .	1·97	1·96	1·78	1·70	1·63
Tar, kilos. . . .	3·90	4·65	5·08	5·48	5·59
Ammoniacal liquor .	4·58	5·22	6·80	8·62	9·86

It will be seen that the coals richest in oxygen contain the largest quantity of water, and also that the proportion of volatile matter increases with the quantity of oxygen. It is well known that the production of gas varies each hour during the distillation of a four-hour charge. The following table shows the percentage yield of gas with each class of coal :—

1st hour . . .	24·9	25·0	24·7	24·1	23·1
2nd hour . . .	29·9	28·4	29·2	29·6	26·9
3rd hour . . .	28·8	28·6	29·8	29·0	29·0
4th hour . . .	16·4	18·0	16·3	16·9	20·7
	100·0	100·0	100·0	100·0	100·0

And if the quantity of all the products by weight be worked out to percentages we obtain the following table :—

PERCENTAGE YIELDED BY WEIGHT OF ALL THE PRODUCTS OF DISTILLATION

Gas	13·70	15·08	15·81	16·95	17·00
Coke	71·48	67·63	64·90	60·88	58·00
Breeze	6·33	7·07	7·41	8·08	9·36
Tar	3·90	4·65	5·08	5·48	5·59
Ammoniacal liquor	4·59	5·57	6·80	8·61	9·86

This table further accentuates the fact that as the oxygen increases so also does the weight of gas, tar, and ammoniacal liquor, whilst, as might be expected, the residual coke falls, and, as is shown by the percentage of breeze, becomes more friable.

The gases evolved by the coals of the five series were analysed, with the following results :—

Carbon dioxide	1·47	1·58	1·72	2·79	3·13
Carbon monoxide	6·68	7·19	8·21	9·86	11·93
Methane and Nitrogen	34·37	34·43	35·03	36·42	37·14
Hydrogen	54·21	52·79	50·10	45·45	42·26
Benzol	0·79	0·99	0·96	1·04	0·88
Olefines	2·48	3·02	3·98	4·44	4·76

And the gravity, make in cubic feet per ton, and candle-power are given in the following table :—

Density of gas	·352	·376	·399	·441	·482
Cu. ft. per ton	10,806	11,116	10,985	10,661	9,856
Candle-power	10·6	12·9	13·5	14·3	14·3

These candle-powers on the No 2 London argand would have been a couple of candles higher.

It will be seen that the carbon dioxide and carbon monoxide increase with the quantity of oxygen contained in the coal,

the methane and olefines also with the oxygen. The illuminating power of the gas is much greater the more highly oxygenated is the coal from which it is produced, but it does not increase so rapidly as the hydrocarbons, because the proportion of carbon dioxide in the gas augments with that of the hydrocarbons.

The coals in classes 1 and 2 yield a good coke and a poor gas, whilst those in classes 4 and 5 give a rich gas and an inferior coke. In practice class 3 is preferred for gas-making because these coals yield good coke, and at the same time a fair quality of gas.

In summing up the results of the experiments, it becomes evident that within a range of 5·5 to 12 per cent. of oxygen, the more oxygen present in a coal, the richer and denser will be the hydrocarbons and the poorer the hydrogen, in the gases evolved from it on distillation.

In speaking of the endothermic character of some coals, mention was made of the very fine research by Constam and Kolbe, which, although it was carried out for a different purpose, gives data which may be utilised for ascertaining how far their results are in accord with those of the La Villette experiments, whilst it has the added charm of dealing with well-known types of English coal, and covers a wider range of composition.

Arranging the nine coals analysed in the order of their percentages of oxygen in the ash- and moisture-free coal substance, we obtain the following table :—

Coal.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.
I. Nottingham, bright . .	81·38	5·30	10·20	2·02	1·10
II. Nottingham, best hard .	83·15	4·97	9·24	2·03	0·61
III. Kinneil	83·99	5·55	9·23		1·23
IV. Yorkshire, Barnsley . .	85·62	4·82	7·92	1·03	0·61
V. Lancashire, Trencherbone	84·85	5·38	7·05	1.87	0·85
VI. Durham, Low Main . .	86·11	5·48	5·66	2·11	0·64
VII. Durham, Ballarat . .	88·64	4·95	4·22	1·77	0·42
VIII. Durham, Hutton . .	88·25	5·46	3·70	1·78	0·81
IX. Welsh Steam . . .	90·10	4·72	2·58	1·53	1·07

Percentage Yield of Products

Coal.	Coke.	Gas.	Tar.	Liquor.	Pitch.	Sulphur Compounds.
I. . .	55·2	18·5	6·7	17·9	1·4	0·3
II. . .	59·7	17·7	8·3	12·7	1·2	0·4
III. . .	63·7	18·5	8·6	6·8	2·0	0·4
IV. . .	70·6	12·9	5·9	8·7	1·6	0·3
V. . .	62·0	20·3	10·2	5·7	1·3	0·5
VI. . .	65·3	17·0	9·2	6·2	2·1	0·2
VII. . .	76·6	12·8	2·5	6·4	1·6	0·1
VIII. . .	68·8	17·5	7·6	3·9	2·0	0·2
IX. . .	80·3	11·2	3·1	3·8	1·3	0·3

Composition of the Gas

Coal.	Carbon Dioxide.	Saturated Hydro-carbons.	Oxygen.	Carbon Monoxide.	Methane.	Hydrogen.	Nitrogen.
I.	2·90	5·25	0·75	7·45	25·35	54·66	3·64
II.	4·15	5·55	0·90	11·49	24·27	49·62	4·02
III.	2·30	5·90	0·50	8·50	29·40	50·20	3·20
IV.	3.50	5·70	0·80	8·27	24·80	51·98	4·95
V.	2·20	7·60	0·60	9·77	28·94	48·08	2·81
VI.	1·70	6·20	0·75	5·02	32·43	50·70	3·20
VII.	1·30	4·45	0·75	2·94	29·78	56·10	4·68
VIII.	0·90	5·85	1·00	3·62	31·20	51·43	6·00
IX.	1·00	2·65	0·80	4·13	24·08	63·04	4·30

The yield of gas in cubic feet per ton, its specific gravity, candle-power, and calorific value, may be tabulated as follows :—

Coal.	Yield Cubic Feet per Ton.	Specific Gravity.	Illuminating Power.	Calorific Value. Gross.	Net.
I.	11,886	·463	7·1	576	517
II.	11,076	·475	6·5	569	509
III.	11,964	·462	9·1	619	554
IV.	9,744	·393	6·2	589	531
V.	12,697	·475	10·2	611	559
VI.	11,674	·433	10·0	627	564
VII.	10,999	·347	6·5	609	547
VIII.	12,253	·427	9·9	647	586
IX.	11,790	·321	2·6	475	100

The illuminating power must be taken merely as a comparison between gas and gas, having been taken in a slit burner at a rate of 5·3 cubic feet per hour.

These two sets of experiments are as good an example as could be adduced of the fallacy of founding ideas and drawing inferences from experimental work made under different conditions. Both sets of experiments are by men whose accuracy and experimental skill are beyond doubt, and yet when you come to compare the two researches it is only in a very few points that anything like agreement exists between them, and the concordant figures of the first set become in the second an almost inexplicable set of anomalies.

The whole of this is brought about by the fact that in the La Villette experiments, at least ten coals of each class were carbonised, and of each of them thirty-five tons were used in three days' working on four-hour charges, so that the anomalies presented by particular coals and minor experimental losses were averaged out, and the results exhibited fairly the characteristics of the class.

In Constam and Kolbe's work, on the other hand, only half a kilo. of coal (1·1 lbs.), was carbonised at a charge, and any abnormal characteristic of the coal or any slight experimental error at once upset the agreement found in the former research.

I am not sure, however, that the abnormal results that crop up under the same conditions do not teach us quite as much if not more than the broader generalisations, and although the average results give us the class distinctions, it is the abnormal exceptions that teach us most as to the individuality of coals.

Before, however, discussing this question it will be well to glance at another set of experiments made, like the La Villette experiments, in the laboratories of the Paris Gas Co., by Euchêne, in his work to establish the endothermicity of coal. He chose for this purpose five coals of the classes laid down

by Ste-Claire Deville, and carbonised them in bulk in a setting of seven retorts.

Class.	Elementary Composition, Ash- and Water-free. Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Volatile Matter.	Coke.	Quality.
I.	88·38	5·06	5·56	1	23·3	75·6	Dense, large.
II.	86·97	5·37	6·66	1	25·9	72·6	Dense.
III.	85·89	5·40	7·71	1	28·3	70·2	Medium.
IV.	83·37	5·53	10·10	1	32·1	65·9	Bad.
V.	81·66	5·64	11·70	1	33·0	64·0	Bad, small.

Composition of the Gas

	Hydrogen.	Methane.	Ethylene.	Benzene.	Carbon Monoxide.	Carbon. Dioxide.	Nitrogen.
I.	54·21	33·37	2·48	0·79	6·68	1·47	1
II.	52·70	33·43	3·02	0·99	7·19	1·58	1
III.	50·10	34·03	3·98	0·96	8·21	1·72	1
IV.	45·45	35·42	4·44	1·04	9·68	2·79	1
V.	42·26	36·14	4·66	0·88	11·93	3·13	1

Here, again, we have the same beautiful accordance of results, hardly a figure being out of place in the analysis of the gases, and one cannot help feeling that they are almost too perfect.

I have pointed out that not only does every seam in a colliery give great differences in the coal, but that the coal from the same seam will often vary so much in composition as to make one doubt its source. From the conditions of its formation it must be so, and, as I have tried to show, the differences in coal are dependent entirely on the proportions in which its main constituents are present in it.

It is useless to go on quoting researches on the composition of coals and the influence which it has on the gases derived from it; but there are one or two points which stand out from all analyses, and which may be taken as generalisations. These are :—

1. The higher the oxygen in the coal, the higher will be the volatile matter. This follows from the fact that the oxygen in the coal is present in the form of both humus bodies and resin bodies, both gas-yielding constituents.
2. The higher the oxygen, the lower will be the coke yield.
3. The higher the oxygen, the larger will be the volume of oxides of carbon in the gas.
4. Oxygen above 10 per cent. or below 4 per cent. means bad coke or non-coking.

CHAPTER VII

TAR : ITS FORMATION, USE, AND DECOMPOSITION

Formation of tar in the distillation of coal—Deposition of tar in the hydraulic main, condensers, and scrubbers—Saturated and unsaturated hydrocarbons—The Paraffin series—Isomerism and metamerism—Naphthenes—The constituents of tar—Benzene and anilin—Naphthalene—Phenol—Creosote oil—Anthracene oil—Effect of oxygen in coal on the tar—Low temperature tar—Course of the decompositions in the distillation of coal—Comparison of tar from Dessau vertical and the horizontal retort—Lewis T. Wright's experiments on the distillation of coal—Utilisation of tar for gas-making and its limitations—Factors governing its successful use—The Dinsmore process—Tully's methane-hydrogen process—Paraffinoid tar—Benzenoid tar—Coke oven tar—Composition of tar from Simon-Carvès and Semet-Solvay ovens—Blast furnace tar—Phenoloid tar—Water gas tar.

The fact that a large proportion of the gas which goes to make up the bulk of coal gas as at present manufactured, is derived from the decomposition of the tar, gases, and hydrocarbon residues left in the coke after low temperature carbonisation, renders a discussion of the composition of these bodies necessary before we can grasp the actions which swell the 3000 to 5000 cubic feet of gas per ton, given by primary decompositions into the 13,500 cubic feet obtained in some of the modern systems of carbonisation.

If coal gas as it leaves the mouth of the retort be allowed to escape through a pet cock, it will be seen to be of a brown colour, and if a piece of white paper be held in the stream of escaping gas it rapidly becomes brown from condensing tar vapour, whilst if the temperature of the retort has been pressed to the highest possible point, the gas will show

greyish black from separated carbon. The brown vapour is formed of myriads of microscopic vesicles filled with coal gas, the envelope being tar, and owing to their lightness they continue to float in the stream of gas until friction or the dashing against some solid body causes them to burst, when the gas is liberated and the condensed tar streams down the surface of the body on which the vesicle has been wrecked, and the result is that although the temperature in the hydraulic main is as a rule well below the condensing point of the tar vapour, only a portion condenses there, the remainder being got rid of in the condensers and scrubbers. Of course, the amounts depositing will vary with the specific gravity of the tar, with the heat of the gases, and even with the composition of the coal, but taken very roughly the proportions would be :—

Hydraulic main	.	60 per cent
Condensers .	.	17 ,,
Scrubbers .	.	23 ,,

If it were not for the tar being mechanically carried forward in this way as a whole, a fractional condensation would take place, the tar constituents of highest boiling point condensing in the ascension pipe and hydraulic main, creosote oils in the condenser, and some of the lightest portions even as far forward as the scrubbers. There is, in fact, a slight tendency in this direction, and when every fraction of a candle-power was jealously watched and guarded by the gas manager, it was realised that sudden cooling of the gas and condensation of tar at too early a period affected the illuminating power more than slow cooling. This is partly due to the tar being thrown out as a whole, whilst with slower cooling some of the benzol is carried away as vapour by the gas. It is also due to sudden cooling and condensation leading to absorption of some of the heavy hydrocarbons from the gas.

The tar in the hydraulic main also shows that some of the more volatile constituents go forward, as it is nearly always thicker than the tar from the condensers, but this is because when condensation takes place in the stream of still hot gas, the condensed portion undergoes a partial distillation, the heavy portions of tar which we find going forward as far as the scrubbers being carried by the skin of the tar vesicles.

The tar from all parts of the purifying apparatus is in ordinary gas practice run into the tar well together with the ammonia liquor, and separating by gravity forms the dark brown or black viscid fluid which we know as gas tar, and which varies in its specific gravity, according to the composition of the coal and the method and temperature of carbonisation, from 1·07 to 1·21.

The same factors which influence the specific gravity of the tar also influence its composition, which is the cause underlying the variation in gravity, and when we come to approach the question of its composition we find ourselves face to face with a question of the greatest complexity, as some one hundred and fifty different compounds containing carbon have been isolated from it.

The chief substances found in it are: Hydrocarbons, oxygenated carbon compounds, and bodies in which sulphur and nitrogen are to be found.

Carbon forms an enormous number of compounds with hydrogen, these bodies being known by the generic name of "hydrocarbons." Twelve parts by weight of carbon will unite with four parts by weight of hydrogen, and when these elements are united in this proportion, the body formed is incapable of combining with chlorine or any other element of the same kind, the constituents having formed what is termed a "saturated compound;" but the compound may exchange the whole or part of its hydrogen for other elements.

Most elements in forming compounds exist only in the

molecule in a very limited number of atoms, but carbon has the property of existing in different bodies to a very large number. Although the simplest compound of carbon and hydrogen known is represented by the formula CH_4, it is only the first of a long series of compounds in which the carbon is saturated by hydrogen, each member of this series containing one atom of carbon and two atoms of hydrogen more than the member of the series preceding it. This series is known as the saturated hydrocarbon or paraffin series, and all its members contain carbon and hydrogen in the ratio of C_nH_{2n+2}.

Besides this series there are many others in which the ratio of carbon to the hydrogen is not so high, and which can therefore unite directly with some other elements, and for this reason are called "unsaturated hydrocarbons." As examples of such series may be cited the ethylene series, having the ratio C_nH_{2n}; the acetylene series, having the ratio C_nH_{2n-2} the benzene series, having the ratio C_nH_{2n-6}.

In the paraffin series the lower members are gaseous, whilst as the molecule becomes more complex they assume the liquid state, and become less volatile and more viscid as the series is ascended, the higher members being crystalline solids. The first four members of the paraffin or saturated series are the gases—

Methane . . .	CH_4
Ethane . . .	C_2H_6
Propane . . .	C_3H_8
Butane . . .	C_4H_{10}

As we have seen, methane occurs in all coal gas, and by volume is the second most important constituent of high temperature gas, whilst as regards heating value and its influence on illuminating power it is the most important.

Ethane is the primary product of the decomposition of the hydrocarbons in coal, and is generally accompanied by traces of propane and butane; but the latter are never present in

high temperature coal gas, and most of the ethane undergoes decomposition at temperatures above 800° C. (1472° F.).

The increase in the number of atoms in the molecules of these gases is reflected by the greater and greater ease with which they can be liquified by cold and pressure. Methane has to be cooled below – 99° C. (– 210° F.) before it can be liquified, ethane can be liquified at 4° C. (39° F.) under a pressure of 46 atmospheres (46 × 15 lbs. on the square inch), propane condenses to a liquid without any extra pressure at – 20° C. (– 68° F.), and butane becomes a liquid at the freezing point, or slightly below. The next member of the group is pentane, which is a liquid so excessively volatile that unless it be kept in well corked-up cans, very little of it will be left in the can after an hour's exposure on a warm day.

With pentane this series of hydrocarbons becomes liquid, and gradually, with increase in the number of carbon atoms, gets more and more viscid, with a higher and higher boiling point, until at about the fifteenth member of the group one arrives at substances which, although still liquid, are so viscid that the fifteenth member is that jelly-like substance known under the name of vaseline. For another five members they are still slightly viscid, and above the twentieth member of the group begin the real solids, a mixture of which constitutes paraffin wax.

The liquid members of the group from pentane up to decane, $C_{10}H_{22}$, have been isolated from coal tar, but although solid paraffin is a common constituent of the tars from shales and even some cannels, a doubt exists as to whether it is ever found in tar from a true bituminous coal.

Of the unsaturated series of hydrocarbons, we find in all coal gas ethylene, C_2H_4, the first member of the ethylene series, in which the ratio of carbon to hydrogen is C_nH_{2n}, and sometimes traces of the next two higher members—propylene C_3H_6, and butylene, C_4H_8, whilst amylene, C_5H_{10}, hexylene, C_6H_{12}, and heptylene, C_7H_{14}, are found in the tar.

If we take acetylene, C_2H_2, and benzene, C_6H_6, we see that the one has a molecular weight of 26 and the other 78; but if we take their percentage compositions they are the same, that is, they contain the same elements in the same proportions by weight. Substances which bear this relation to each other, but possess different properties, are said to be "isomeric." When substances have the same percentage compositions but different molecular weights, as in the case of acetylene and benzene, they are said to be "polymeric," whilst compounds that agree both in percentage composition and molecular weight are said to be "metameric." The wide differences in physical and chemical characteristics which may exist between "metameric" compounds are due to the different relations which the atoms forming the compounds bear to each other.

There is a class of, but little known, hydrocarbons metameric with the ethylene series, that is, represented by C_nH_{2n}, and having the same percentage composition. These bodies are called the naphthenes or hexahydrides. They are found in Russian petroleum. Renard found them in the products of distillation of rosin, and Armstrong and Miller isolated members of the group from the deposit of liquid hydrocarbon produced on compressing oil gas, and these observers named them "pseudolefines." These bodies are abundant in low temperature coal tar, and three members of the group have been isolated from coal tar :—

Hexahydrobenzene .	C_6H_{12}
Hexahydrotoluene .	C_7H_{14}
Hexahydroisoxylene .	C_8H_{16}

These bodies differ from members of the ethylene group in their behaviour when decomposed by heat, the ethylenes breaking up into simpler hydrocarbons, whilst the hexahydrides merely shed off hydrogen and become converted into benzene, C_6H_6, toluene, C_7H_8, and xylene, C_8H_{10}, re-

spectively, and there is very little doubt, but that the benzene and some of the other aromatic hydrocarbons found in high temperature tar, and which occur only in very small proportions in low temperature tar, are partly formed in this way.

Hydrocarbons of this character have also been isolated from coal, and it is probable that the benzene occasionally found in low temperature gas has been formed from their decomposition, as the temperatures employed have been too low for any of the other actions that give rise to benzene.

The other chief constituents present in coal tar may be tabulated as follows :—

Neutral Hydrocarbons.		Boiling Point. ° C.	° F.	Formulæ.	Specific Gravity.
Liquid	Benzene	80	172	C_6H_6	0·88
	Toluene	110	230	C_7H_8	0·87
	Xylene	142	288	C_8H_{10}	0·87
	Isocumene	170	332	C_9H_{12}	0·85
Solid	Naphthalene	217	423	$C_{10}H_8$	..
	Anthracene	360	680	$C_{14}H_{10}$	..
	Chrysene	..	..	$C_{18}H_{12}$	..
	Pyrene	..	..	$C_{16}H_{10}$	..
Alkaline products :—					
Ammonia		..	..	NH_3	..
Anilin		182.5	367	C_6H_7N	1·02
Picoline		130	266	C_6H_7N	0·96
Quinoline		239	462	C_9H_7N	1·08
Pyridine		117	243	C_5H_5N	..
Acids :—					
Carbolic acid		180	366	C_6H_6O	1·07
Cresylic acid		..	..	C_7H_8O	..
Rosolic acid		..	..	$C_{19}H_{14}O_2$	..
Brunolic acid		..	..	..	..
Acetic acid		118	234	$C_2H_4O_2$	1·06
Free carbon.					

In roughly considering the proportions in which the main constituents occur in high temperature coal tar, we can still further simplify the composition, and look upon it as containing benzene, naphtha, naphthalene, anthracene, carbolic acid, and pitch; and if this tar be carefully redistilled, we find it can be separated into the constituents which distil over at various temperatures.

First, light oils pass over, from which benzene and its homologues can be obtained; then heavy tar oil, from which carbolic acid is made; and pitch is left, from which a substance called anthracene can be separated. The benzene obtained is the source from which anilin is prepared; and it is from anilin that most of the coal-tar colours are derived.

When benzene is acted upon with strong nitric acid, nitrobenzene, $C_6H_5NO_2$, is formed. On treating this with dilute sulphuric acid and zinc dust, or acetic acid and iron filings, hydrogen is evolved, and in its nascent state attacks the nitrobenzene and removes its oxygen, leaving behind the compound of carbon, hydrogen, and nitrogen called anilin, $C_6H_5NH_2$. It is from anilin that the brilliant colours mauve, magenta, and other purples and reds are produced, by acting upon it with oxidising agents; and from it can also be obtained the beautiful series of anilin yellows, blues, and violet.

The naphthalene that used to be used in the albo-carbon system of enriching gas, and which is now largely employed as disinfecting tablets and also as a source of other coal tar colours is prepared from coal tar, which is distilled. The first portion consists of light oils, naphthas etc., whilst the second portion is rich in phenols and cresols. The second distillate is again distilled, and the residue left becomes semi-solid, owing to the separation of naphthalene, which on standing collects and cakes on the top of the oil. This is then removed, and pressed by hydraulic power in a hot

press, each plate of which contains a steam pipe to heat it. The crude naphthalene so obtained is then redistilled; but it still contains a number of impurities, which would cause it to turn yellow. To get rid of these it is melted, and forced by steam pressure into a steam-jacketed cylinder, where it is washed in dilute alkali to get rid of the phenol, and four times with strong sulphuric acid, to remove sulphonates, meta-naphthalene, etc. It is then water-washed free from acid. These washings take about seventy-two hours. The naphthalene then undergoes a final distillation, after which it is melted in steam-jacketed coppers, and is ladled out and cast into sticks, blocks, or tablets, according to the use to which it is to be put.

The distillate from the residue, rich in napthalene, contains those invaluable disinfectants, carbolic acid or phenol, C_6H_6O, and cresol or cresylic acid, C_7H_8O, and the method now usually employed for their separation is to take the distillate from the tar that comes over between 210° and 240° C. (410° and 464° F.), and which is generally known as "carbolic oil," and to heat it with a hot saturated solution of potassium or sodium hydrate. After it has been well agitated the mixture is allowed to stand for four hours, when the alkaline solution containing the carbolic and cresylic acid separates, and is drawn off and neutralised with sulphuric acid. The crude carbolic acid rises to the surface, and is skimmed off and purified by fractional distillation and crystallisation.

The fraction that distils over from the tar between 240° and 270° C. (464° and 518° F.) is known as "creosote oil," consists of a mixture of the higher homologues of phenol with various hydrocarbons, and is largely used for treating timber, such as railway sleepers, etc., which have to withstand the action of decay.

The fraction of the tar distilling at 270° to 320° C. (518° to 608° F.) is called "anthracene oil," and is the source from which anthracene, $C_{14}H_{10}$, is obtained in crystals by cooling,

and is the starting point from which the beautiful series of alizarin colours are derived.

It has been estimated that from the tar yielded by a ton of good gas coal there can be obtained :—Half a pound of magenta, which will dye 375 square yards of material ; one and a half pounds of carbolic acid ; six and a quarter pounds of naphthalene ; half a pound of anthracene ; besides a host of minor products used as medicines, as developers in photography, sugar substitutes, etc., so that during the last century tar has proved itself to be a veritable happy hunting-ground for the chemist. In colouring matters alone over three hundred owe their source to this black viscid product of destructive distillation.

The chemical composition of the coal exerts a considerable influence on the composition of the tar, and Ste-Claire Deville, as the result of the La Villette experiments, came to the conclusion that " the higher the percentage of oxygen in the coal, the more tar and ammonia are formed, and the more hygroscopic moisture is contained in the raw coal. There is no doubt that this is true as long as the hydrogen is above 5 per cent. and the oxygen does not exceed 12 per cent.

Dr Bunte, in a series of experiments made on German coals in 1886, found the following ratios for the oxygen in the coal, and the amount of tar formed by carbonising them under ordinary gasworks conditions.

Oxygen in the Ash- and Moisture-Free Coal.	Kilos. of Tar per 100 kilos. of Coal Carbonised.
13·04	5·22
11·64	5·79
10·13	5·33
8·27	4·09

It is seen from this that the quantity of tar rose with increase of oxygen up to 11·64 per cent., but showed a falling

off above this amount, whilst as soon as a coal more in the nature of a cannel was used, containing 7·27 per cent. of hydrogen, the amount of tar became largely increased, although the oxygen was under 11 per cent.—

10·78 8·81

Many of the modern experimentalists have determined the tar produced from coal of various compositions, but unfortunately they have worked with small quantities of material, varying from a kilo. to a gram. Small scale experiments of this kind are useless as far as the volume of tar is concerned from a working point of view, as in these experiments the tar vapour escapes freely directly it is formed, with the result that a yield of tar considerably above that obtained in practice is produced, whereas in practical working the tar vapour distils forward into the cool mass of coal and condenses there, to be in part redistilled as the heat reaches it, leaving behind pitch as a luting material in the mass. From results on a large scale, however, it is quite clear that when a coal of the flaming class is being distilled a large proportion of tar is undoubtedly formed, but of a weak and watery character, owing to the fact that the volatile matter in such a coal contains a larger proportion of humus bodies than of the resinous and hydrocarbons. If, however, a coal contains 10 to 11 per cent. of oxygen, and at the same time hydrogen well above 5 per cent., it is an indication that the oxygen in such a coal is there largely as resinous bodies, and the tar distillates are in consequence high and rich in heavy hydrocarbons.

It is to be noted that the composition of the tar also as well as the quantity is affected by the constitution of the coal bodies, and I have noticed that with low temperature carbonisation a coal rich in oxygen invariably gives a tar rich in phenol and cresol, and in a series of low temperature distillations of various coals, made by Bornstein, he found

that with high oxygen he obtained large proportions of oxygenated compounds like phenol and cresol, but at the same time the paraffins were low.

We have already seen that the percentage of hydrogen present in the coal is a strong indication of its character; percentages above five showing preponderance of resin bodies, whilst when the hydrogen falls much below five, and the coal is rich in oxygen, it is chiefly humus bodies that are present. As it is liquid products of destructive distillation of resin bodies and hydrocarbons which yield the coke-binding material and richest tar, it is evident that when the oxygen has risen to the point that indicates a high humus content, a poor tar will always be found. A very good proof of this is that, directly the humus and consequently the oxygen gets above a certain limit, the coal becomes non-coking.

Tar, as made in the manufacture of gas, that is, at temperatures between 900° and 1000° C. (1652° and 1832° F.), is a product which bears very little resemblance save in colour to the liquid products that first distil from the coal, being built up largely of the products of secondary reactions taking place at the high temperature of the retort, such actions being responsible for the formation of the naphthalene, and many of the aromatic hydrocarbons. If the temperature falls, owing to bad furnace arrangements, to between 600° and 800° C. (1112° and 1472° F.), then these secondary actions are checked, and members of the saturated and naphthene series of hydrocarbons begin to make their appearance. These so complicate the separation of the benzene and other valuable constituents of the tar that the distiller fights shy of them, and the gas manager gets the idea that low temperatures ruin his chief liquid residual. If, however, the temperature be dropped to between 400° and 500° C. (752° and 932° F.), the character of the tar alters entirely.

The tar varies in quantity with the coal used, and is sometimes as high as 23 gallons per ton, and in most cases

averages 20 gallons. This low temperature tar is very distinctive in its characteristics. It has a specific gravity of about 1·075, is very liquid, and contains an abundance of light solvent oils, very low aromatic hydrocarbons, very little phenol, but large quantities of cresol, no naphthalene, and very little anthracene, whilst the free carbon is as a rule below 2 per cent.

The very low percentage of benzene in the light oils is made up for by the presence of paraffins, such as hexane, heptane, and octane, whilst there are also present considerable quantities of naphthenes, hexahydrides, or hexa-hydro-benzenes.

Carbolic acid occurs in very small quantities, but its higher homologues, such as cresylic acid, etc., occur in much larger quantities than in coal tar. There are also present quantities of polyhydric phenols, or other esters of the type met with in coal tar, which form resinous masses difficult to investigate. The pitch left as a residue amounts to about 40 per cent. of the tar, and is of very fine quality, owing to the practical absence of free carbon.

The average tar yielded by coal carbonised between 400° and 500° C. (752° and 932° F.) gives on distillation the following results.

Specific gravity . . 1·073

Distillation on 2274 cc. (0·5) Gallon

		Per cent. by vol. on Tar.	Specific Gravity.	Volume of Hydro-carbons.	Tar Acids recovered.
Water .	..	2·64	..	..	..
Light oil, to	170° C.	3·10	·844	3·10	..
Carbolic oil,	170°-225°	13·72	·959	8·62	4·8
Creosote oil,	225°-240°	8·35	·9885	4·64	3·1
	240°-270°	8·35	·9923	5·45	2·55
Anthracene	270°-300°	8·80	1·029	6·60	1·76
	300°-320°	12·31	1·033	8·80	3·10
Pitch, by weight on vol.		..	41·71	..	..
Bases recovered		..	1·32	..	..

Light Oils

Percentage distilling below—			Calculated on Tar.	
100° C.	15·6 by vol.		0·55	
120°	31·2		1·09	
140°	54·7		1·91	
170°	82·8	100·0	2·90	3·10
Over 170° and loss	17·2		0·20	

The ammonium sulphate amounts to only 12 lbs. per ton of coal, the temperature being too low for large production.

From these results it seems more than probable that the primary products of decomposition of the coal are those which are produced during the actions taking place in its formation, *i.e.* methane, carbon dioxide and water, plus those compounds formed by the rising temperature and consisting of the first nine or ten members of the paraffin series, naphthenes, and oxygenated hydrocarbons like cresylic acid. The action of heat upon these starts at once secondary reactions, and gives us gaseous and liquid compounds identified in low temperature gas and tar, whilst at higher temperatures these in contact with the highly heated coke envelope of the decomposing coal undergo further actions, analytic and synthetic, and becoming diluted with poor gas from the residual pitch left in the low temperature coke, yield the high temperature coal gas and tar.

The gradual alteration in the character of the tar with rise of temperature is well shown by analyses made by Lewis T. Wright of the tar obtained by distilling a Derbyshire coal at temperatures varying from 600° C. (1112° F.) to the ordinary retort temperature :—

Coal Employed

Carbon . . .	81·92
Hydrogen . . .	5·39
Oxygen . . .	6·88
Nitrogen . . .	1·28
Sulphur . . .	1·97
Ash	2·56

Yield of gas, c. ft. per ton .	6,600	7,200	8,900	10,162	11,700
Specific gravity of tar . .	1·086	1·102	1·140	1·154	1·206
Composition of tar by weight :—					
Ammoniacal liquor	1·20	1·03	1·04	1·04	0·383
Crude naphtha .	9·17	9·65	3·73	3·45	0·995
Light oil . .	10·50	7·46	4·47	2·59	0·567
Creosote oil .	26·45	25·83	27·29	27·33	19·440
Anthracene oil .	20·32	13·57	18·13	13·77	12·280
Pitch . .	28·89	36·80	41·80	47·67	64·080

This table illustrates very strikingly the changes which took place in the tar in the first few years of the century, when the gas manager, having to deal with a reduction in the illuminating standard imposed by Parliament on his gas, attempted to do so by pressing the temperatures to as high a point as possible with six-hour charges, and as a result made tar which was but little more than creosote oil, naphthalene, and pitch. The former analyses do not show the important fact that in the pitch the free carbon rose from 2 per cent. in the low temperature tar to over 30 per cent. in that obtained at the highest temperatures.

A very interesting point in this investigation was that the five samples of crude naphtha were analysed for paraffins, with the following results :—

Specific Gravity of Tar.	Percentage of Crude Naphtha by volume.
1·086	5·0
1·102	4·0
1·140	1·5
1·154	1·0
1·206	1·0

which again brings out the fact that the paraffin series are probably primary products of the decomposition of the coal; and this is further confirmed by the fact that when coal is distilled under reduced pressure it exhibits the same characteristics as low temperature tar.

The new methods of carbonisation, in heavy charges, vertical retorts and chambers, have made a great improvement in the quality of the tar, by allowing the first two-thirds of the charge to distil under conditions which provide a cool escape for the tar vapours. Mr Drury has given the composition of tar from Dessau verticals as used at Sunderland in comparison with tar from horizontals, as follows :—

	Vertical.	Horizontal.
Specific gravity . . .	1·113	1·220
Free carbon	4·0	17·25 by weight
Tar acids	5·3	3·0
Distillate—		
up to 170° C. . . .	13·0	4·9
„ 270° . . .	24·0	18·4
„ 350° . . .	9·0	9·0
Pitch	50·0	60·6

Mr J. G. Newbigging contrasts tar from the Glover-West continuous vertical installation at Manchester with tar from horizontals as follows :—

	Vertical.	Horizontal.
Specific gravity . . .	1·074	1·193
Free carbon	3·1	17·67
Distillate per cent. by vol. —		
up to 170° C . . .	9·1	4·5
„ 270° . . .	25·7	12·0
„ 350° . . .	24·9	19·5
Pitch, by weight . . .	46	57·0

The tar from fully charged horizontals shows an equally great improvement of the same character.

It has always been felt by the gas engineer that tar meant a great waste of vapourised carbon, which, if it could be kept in the gaseous form, would give an enormous addition to the gaseous products, and would represent a large proportion of heat and light. Experiment, however, has shown that the gasification of tar and tar oil is a most thankless task to undertake, and most gas engineers look upon it from the point of view taken by Lewis T. Wright—that tar is a child of high temperature, born in the heat of the retort, and so thoroughly acclimatised as to resist all further attempts to gasify it successfully.

As regards the chief portions of high temperature tar—pitch, naphthalene, and the higher aromatic hydrocarbons—this is true, but, as we have seen, lowering the temperature of distillation increases the yield of tar, and it seems clear that a large proportion of it is due to primary action, and consists of paraffins, naphthenes and other hydrocarbons, which would lend themselves to gasification, as well as the oxygenated and "cycle" derivatives which are more resistant, whilst naphthalene, anthracene, etc., are absent. It is evidently worth while to see how far tar of this character can be gasified, and whether it is economically better to do this than to utilise it for other purposes.

In the early 'eighties, Lewis T. Wright made a number

of experiments on the gasification of tar and tar distillates by passing them into a retort filled with lime and heated to 1100° C. (2012° F.), and obtained the following results :—

Tar . . .	10,700 cub. ft. per ton of 12·5 candle-power gas.				
Crude Naphtha .	10,130	„	„	20·5	„
Up to .	27,000	„	„	14·5	„
Light Oils . .	18,000	„	„	16·0	„
Up to .	30,000	„	„	13·5	„
Creosote Oil .	13,300	„	„	14·00	„
Up to .	29,300	„	„	8·5	„

Now, tar in those days *was* tar, and not creosote oil, pitch, naphthalene, and free carbon, and yet on these figures it was decided that tar as a source of gas was "dear at a gift," owing to the ubiquitous naphthalene obstructions and troubles that followed any attempts at gasification.

I have made many experiments upon this subject, and the conclusions to which I came long ago were that tar, once obtained in the liquid state, could be utilised for the purpose of gas-making only in one of two ways :—

1. Distil off the naphthas, light oils, etc., which come over below 240° C. (464° F.), and gasify these ; or

2. Inject the tar into a mass of incandescent coke, so as to break it up into hydrogen and methane, having a sufficient column of red-hot coke to filter off the deposited carbon.

If the ton of coal yields at low temperatures 20 gallons of 1·07 specific gravity tar, it is found that 25 per cent. of it will distil below 240° C., leaving a residue perfect for road-making. The 25 per cent. of distillate represents about 50 lbs. weight, and on gasification will yield 10 cubic feet per lb. of 15 to 16 candle-power gas, and therefore by this method there is obtained an addition to the gas from the ton of coal of 500 cubic feet of good lighting and heating gas, and 15 gallons of good road-making tar.

If on the other hand the tar be returned into incandescent coke so as to decompose it entirely, the 20 gallons will yield 1500 to 2000 cubic feet of a mixture of hydrogen and methane with oxides of carbon, having a thermal value of between 400 and 450 B.Th.U.

Taking the tar, even of the quantity and quality yielded by such a process, no economy is to be found in converting it into gas by any other than the most simple expedients of the same character as the one utilised by Settle, of simply returning it to the retort. This applies to tar after it has been condensed, and not to nascent tar in the gaseous state as it leaves the decomposing coal.

At the beginning of the last century, when Clegg, Malam, and others had grasped the importance of preventing the degradation of the gases by contact with hot carbon, and were trying to avoid it by carbonising in thin layers, it was commonly believed that if coal were distilled in layers less than two inches in thickness no tar was formed. This, of course, is nonsense, as any one can see by heating a gram of coal in the bottom of a test tube ; but under the conditions of their experiments none or very little came over, and the reason is the same that led to little or no tar being found in the Settle vertical retort.

In Clegg's web and rotary retorts a thin layer of coal was passed in a tray or on a web through a flat oven heated to a high temperature, which gave an enormous ratio of radiant surface to the weight of coal carbonised, and under these conditions the nascent tar vapours never had a chance of condensing into the vesicular form found in the brown tar vapour leaving the retort. It was superheated instead of being cooled, and bore the same relation to brown tar vapour that superheated steam does to the condensing steam we see leaving the spout of a kettle. Catch it in this nascent state and heat will gasify it, but if it once cools to brown vapour molecular condensations prevent it ever again being got in the

gaseous state without almost complete decomposition. The tar must pass direct from the coal into a temperature higher than that which gave it birth, but not hot enough to do more than gasify it, and if any important results are to be obtained from tar as a gas producer it will be on these lines, and carried out in a vertical retort, so that the radiant heat alone acts, and contact is reduced to a minimum.

One of the most elaborate attempts to utilise the tar for gas-making was the Dinsmore process, in which the coal gas and the vapours which, if allowed to cool, would form tar, were made to pass through a heated chamber, and a certain proportion of otherwise condensible hydrocarbons was thus converted into permanent gases. Using a poor class of coal, it was claimed that 9800 cubic feet of 20 to 21 candle gas could be made by this process; whilst by the ordinary process 9000 cubic feet of 15 candle gas would have been produced.

In the centre of each bed of six retorts, an empty retort, called the "duct," was fixed, and through this the whole of the gas and vapour produced in the other retorts had to pass before reaching the hydraulic main. The duct was kept at a bright cherry red heat (1700° F. = 926° C.), at the entrance, and at a dull red at the exit end (1200° F. = 639° C.), this gradation of heat being important, as if it were at a high heat throughout the hydrocarbons would have been over-cracked, and a loss of illuminating power would have been the result.

From the duct an ascension pipe led the gases to the main by means of a bridge pipe, and this ascension pipe was provided with a water jacket, which caused liquid tar to condense and render any condensed pitch or carbonaceous matter sufficiently liquid to slide back down the pipe, and so prevented any chance of choking.

Each retort in the bench, besides having a connection with the duct, was also connected with the hydraulic main in the

usual manner, but closed by a heavy seal. One retort of the bed of six was drawn and charged hourly, and as each retort was heated for six hours, and as the products of distillation vary according to the period for which the retort has been heated, this arrangement kept the average composition of the gases mingling in the duct fairly constant.

The quantity of tar produced by this process was roughly about two-thirds of the quantity made in the ordinary way, and was moreover very poor in light oils and tar acids, so that there can be but little doubt that the hydrocarbons and phenols were broken down into olefines and acetylenes.

On analysis the Dinsmore gas gave the following composition :—

Carbon dioxide . . .	0·23
Illuminants . . .	6·76
Carbon monoxide . .	8·10
Methane	40·34
Hydrogen	43·98
Nitrogen	0·59
	100·00

Specific gravity . .	0·428
Illuminating power . .	22·3 candles
Carbon density . .	2·96
Hydrogen density . .	5·80

In distilling the coal in the ordinary way the yield of tar was 11 gallons per ton, but by the Dinsmore process only 7 gallons. On examining the analysis of the ordinary and Dinsmore tar, it is at once evident that the four gallons which have disappeared are the chief portions of the light oils and creosote oils ; and these are the constituents which gave the increase of illuminating power to the gas.

The economic advantage of gasifying tar is purely a question of the price the tar commands. Supposing the tar could be so gasified, and yielded 120 cubic feet of gas per gallon of 12 to 14 candle-power gas, it would not be worth more than 10d. per thousand in the holder, so that unless the price of tar is under a penny a gallon, it would not pay to use it for this purpose.

Another method for the possible utilisation of tar is to break it up entirely by injecting it into a column of incandescent coke, when it becomes decomposed into carbon, oxides of carbon, methane, and hydrogen. It is practically impossible to do this under any ordinary condition of decomposition, owing to the deposition of free carbon luted together by heavy pitch, which, as before noted, has in all attempts at gas-making from tar led to disaster.

Mr C. B. Tully has got over this difficulty by making a generator in which the fuel column is nearly double that found in a carburetted water gas generator, and three times more than that in a blue water gas generator. It is the lower portion only of this which is raised to incandescence, by an air blast introduced through openings in the lower part of the generator. About midway up the firebrick lining nostrils connect with a flue passing entirely round the generator and opening into a stack pipe which is closed at the top by a snift valve. In this way the incandescent portion of the fuel is maintained at a definite height, as the products of the "blow" pass away through this flue, whilst the upper portion of the fuel is raised only to a moderate temperature.

When the necessary incandescence of the fuel has been attained, the air blast is shut off and the snift valve closed, and the exhauster is started. At the same time tar is injected into the fuel from the clear space below a projecting ring in the firebrick lining between the flue and the air injectors, and steam also is turned on at the bottom of the generator. This steam is directed upon the clinker and

serves to break it up, and, passing upwards, is then converted into water gas. The tar gets broken up into carbon and gaseous products containing a large proportion of methane, and these, mingling with the water gas formed from the steam, pass upwards through the generator. The carbon is filtered out by the cool charge above, and is used up as the fuel gradually sinks into the zone of combustion.

The gas which finally leaves the generator is a mixture of hydrogen, carbon monoxide and methane, with a very small percentage of carbon dioxide. From the generator the gas passes through the scrubber into the condenser to the exhauster, which forces it into the holder.

Methane-hydrogen, as the gas is called, differs from water gas in many respects. It burns with a yellow instead of a blue flame, due to the large volume of methane present, and the percentage of carbon monoxide is very much less. An anaylsis of methane-hydrogen made from coal gas tar gave the following results :—

Carbon dioxide . . .	2·8
Carbon monoxide . .	28·8
Unsaturated hydrocarbons .	0·8
Saturated hydrocarbons .	19·2
Hydrogen	42·4
Oxygen	0·2
Nitrogen	5·8

The gas, owing to the quantity of the hydrogen and methane present, has a satisfactory thermal value.

We have seen the wide differences existing between low temperature tar and high temperature tar, and that these are due to the low temperature product containing a large proportion of " paraffin " hydrocarbons, and but little benzene and toluene, whilst the high temperature tar is rich in the aromatic hydrocarbons, benzene, toluene, etc., and the paraffins are in such small quantities as to be almost negligible.

For this reason tars of the low temperature type are called "paraffinoid" tars, and those made at high temperatures from thin charges of coal are termed "benzenoid" tars. When, however, a mass of coal is carbonised, no matter how high the retort temperature, the heat penetrates the mass only slowly, so that the carbonising action is taking place at the lowest temperature at which the coal is affected by heat, and if the vapours can escape without too much contact with the exterior red-hot mass, they begin at once to show paraffinoid characteristics, and as the presence of paraffins makes it difficult and expensive to extract the pure benzol, tar of this character is not appreciated by the tar distiller, who has in view products for the colour industry. On the other hand, the higher tar acids found in the paraffinoid tar render them invaluable where liquids for disinfectants and for preserving timber are desired.

We have seen already that the newer methods of carbonisation, owing to increase in the bulk of the charge, all have a tendency to increase the paraffinoid character of the tar yield, but these tars still retain many features of the old small charge tar, owing to the earlier portions distilled yielding low temperature paraffinoid tar, and the later portions having to pass through the hot outer crust of the charge, yielding "benzenoid tar," so that the finished product is a mixture of the two.

As the new methods of carbonisation become generally adopted, the benzenoid tar that characterised the nineteenth century will gradually disappear, and the supply of benzene will naturally be reduced; but this will affect the colour industry but little, as it is centred in Germany, and they obtain most of the benzene from coke oven gas, whilst the new type of tar still contains plenty of anthracene.

As the bulk of the charge affects the character of the tar, one would expect to find a considerable difference between coal tar as produced by horizontals worked under the old

conditions and coke oven tar from the modern recovery plant. In the coke oven the mass of coal carbonised is far larger than in any retort process, and as the travel of heat into it is in consequence much slower and the temperature maintained for a longer period, one would *a priori* expect an even larger proportion of primary products in both gas and tar, but a further consideration of the question shows several factors that would militate against this.

In the first place, crushed coal is used. In the next, the charge is fed into the chamber under pressure, and is generally wet, whilst the temperature in the upper part of the chamber is higher than in a retort, and the mass through which the gas and tar vapour have to find their way is much greater.

The improvements in modern carbonisation are due, as we have seen, to two causes—(*a*) distillation at low temperature as the heat passes slowly into the mass, and (*b*) a cool exit for the products. Although in the coke oven we have the first condition, the second is wanting, and the wet compressed mass of smalls, by hindering the passage of the gas and vapours, drives more of it into hotter zones, in which both gas and tar vapour become to a large extent degraded and more aromatic hydrocarbons formed, so that coke oven tar is nearer to the lightly charged horizontal retort tar than to the modern more paraffinoid tar.

A sample of tar from Simon-Carvès ovens, as analysed by Watson Smith, gave :—

Below 120° C.	6·2	per cent	water by vol.
210°	1·6	,,	naphtha.
210°	2·9	,,	oil.
220°	1·3	,,	oil.
230°	0·5	,,	naphthalene.
300°	18·6	,,	naphthalene, anthracene, and oil.
Above 300°	34·2	,,	anthracene and oil.
Residue	30·5	,,	half-coked pitch.

Another sample after redistillation and treatment gave :—

Water	10·00
Benzol	0·50
Solvent naphtha	0·60
Heavy naphtha	0·40
Crude carbolic acid	0·05
Creosote oil	46·50
Anthracene	0·74
Pitch	41·21

A fair average yield from a modern coke oven is 4·5 per cent. of tar, or roughly nine gallons, so that in quantity it is a little less than from gas manufacture.

A more recent analysis from Semet-Solvay coke ovens gives the following results :—

Specific gravity, 1·170.

	Per cent.
Light oil, 80°–170° C.	3·7
Middle oil, 170°–230° C.	9·8
Creosote oil, 230°–270° C.	12·0
Anthracene oil, over 270° C.	4·3
Pitch	67·0
Water	2·3

The tar obtained by distilling coal in a vacuum, or rather under largely reduced pressure, has all the characteristics of the low temperature tar obtained in the manufacture of coalite, which confirms the view that the constituents that give these tars a "paraffinoid" character are primary constituents.

Another source of coal tar, or rather tar from coal, as it varies in composition widely from the tars yielded by the gas industry and coke ovens, is blast furnace tar. In most blast furnaces for the production of pig iron only the best metallurgical coke is employed, as the fuel has to be built up with alternate layers of iron ore to a considerable depth in the

furnace, and it has to bear a considerable crushing strain as well as the attrition during the sinking of the charge in the furnace.

It is manifest that an ordinary bituminous coal could not be used for this purpose in place of coke because, as the heat reached it, softening and caking of the mass would take place, and as the temperature rose arches of coke would form and upset the whole working of the furnace. In certain parts of the west of Scotland, however, there are large deposits of what is known as splint coals, which are flaming coals rich in oxygen and which do not soften, cake, or swell when heated, but yield a fairly hard coke, of the same size and shape as the original coal, and a number of Scotch iron works and a few north of England works use this coal direct in the blast furnace, as it cokes as the heat reaches it and answers well in practice. The following analysis of such a coal will give an idea of the composition :—

Splint Coal

Carbon . . .	70·05
Hydrogen . . .	5·24
Oxygen . . .	12·08
Nitrogen . . .	1·36
Sulphur . . .	0·75
Ash	6·72

Up to 1880 the gas and tar distilling from the top of these furnaces burnt to waste, but about that date attempts began to be made to fit the top of the furnace with a counter-balanced cone, which allowed the charges to be shot into the furnace but prevented the escape of tar and gas, which were led off through an exit pipe just below it, and allowed the recovery of tar and ammonia and the utilisation of the gas for power purposes.

Watson Smith, who has probably done more good work on the composition of English tars than any other observer, gives the composition of blast furnace tar as follows :—

Specific gravity, 0·954.

		Volume.	Weight.	Sp. Gr.
Distillate below 230° C.	water . .	30·60	32·3	1·007
	oil . .	2·91	2·8	0·899
230°–300° C. . . .		6·97	7·1	0·971
300° until oils solidify .		13·02	13·5	0·994
Paraffin scale		16·75	17·3	..
Coke		..	21·5	..
Loss		..	5·5	..

As might be expected from the high oxygen in the class of coals used, the tar contains a large proportion of phenols. Indeed, it used to be known as " phenoloid tar," only small traces of toluene, xylene and naphthalene being present, whilst benzene and anthracene are absent. The carbolic acid and cresol are low, but the phenols of higher boiling point are abundant.

I made many attempts to crack this oil in such a way as to yield illuminating gas but failed. It is, however, largely used for pickling sleepers, and also in spray lamps of the Lucigen type.

A tar which, although not derived from coal, is often met with in gasworks is " water gas " tar, formed by the cracking of oil in the carburetting of water gas, an analysis of which is given by Matthews and Goulden as follows :—

Benzene . . .	1·19
Toluene . . .	·83
Paraffins . . .	8·51
Solvent naphthas . .	17·96
Phenols . . .	trace
Middle oils . . .	29·14
Creosote oils . . .	24·26
Naphthalene . .	1·28
Anthracene . . .	0·93
Coke	9·80

CHAPTER VIII

COKE

The formation of coke—Distinction between retort and oven carbonisation —Characteristics of good coking coal—Effect of oxygen on the coking properties of coal—Work of Anderson and Roberts on the coking of coal—Temperature of the formation of coke—Burgess and Wheeler's experiments on low temperature coke—Nature of the luting material in coke—Probable true cause of the binding—Effect of rate of heating on the coking of coal—Parry's researches on the gases in coke—Analysis of the ash of coals—The effect of temperature on the appearance of coke—Beehive coke—Coking in ovens—Properties of the coke yielded by various coals—Reasons for the coking of coal—Metallurgical coke—Gas Coke—The use of coke as a domestic fuel —Smoke production—The burning of coal in an ordinary grate—Special forms of grate—The distribution of heat in a domestic fire—Drawbacks to the use of coke as a domestic fuel—Low temperature coke—Coalite—Coalexld—Charco.

Coke is the name given to the solid residue left by the destructive distillation of coal and many other carbonaceous substances, and contains as its chief constituent carbon, together with the mineral matter or ash of the original body, such portions of the residues as the temperature employed has failed to drive out of the mass, and occluded gases.

Many points with regard to the character of the coal and the coke formed from it have been of necessity already mentioned in discussing the composition of coal and other subjects connected with it, but in passing the whole subject under review it will be necessary to refer again to several of these.

The whole end and aim of carbonisation is to obtain as much as possible of the energy stored in coal in the con-

dition most applicable to the uses for which it is to be employed. As these vary over a very wide range, practical experience has led to the destructive distillation of coal being carried out mostly under two distinct sets of conditions—the one aiming at obtaining the maximum result from the gaseous products, and the second at obtaining the best possible coke.

Of late years many attempts have been made to bring into line the two great industries of gas-making and furnace coke production (both dealing with the destructive distillation of much the same class of coal) ; but in most cases a lack of appreciation of the principles underlying the complex actions taking place during carbonisation has proved an obstacle to any important advance—each industry viewing the problem from its own particular standpoint, and failing to grasp the wide differences between substances made as the result of a process designed for their special production and the same bodies when they are made as a by-product. And even now that a process of gradual evolution has led to carbonisation in bulk being carried out in practically identical forms of apparatus, *i.e.* the Continental chambers for gas making and the by-product recovery coke oven for coke, yet the same factor has led to totally different practice.

Furnace coke, as an example, must have certain characteristics to fit it for metallurgical work, which cannot be obtained in the ordinary processes of making good illuminating gas ; whilst if the gas is to satisfy the parliamentary requirements laid down for most large town supplies, it is useless to expect to obtain the same volume of it from a coke oven that you would from a gas retort. So that whilst the gas manager hankers after the economies incidental to carbonisation in bulk, he is constrained to work with much smaller charges in order to obtain the necessary quality and quantity of gas ; and although he uses temperatures quite as high as the coke oven manager, he misses the factors of time and mass that are necessary for a good furnace coke.

Coke is made by the gas manager for the simple reason that he cannot make gas without having coke left as a residue ; and as he devotes but a small portion of his attention to its quality, it is evident that it will not be as good as the product of the coke oven, to the properties of which every care has been given. However made, coke has certain marked physical and chemical characteristics, which are dependent upon the nature of the coal used, the temperature employed in carbonisation, and the rapidity with which the heating has been carried out.

We have seen that it is only certain classes of coals that on carbonisation yield a coherent coke, and that when a coal contains less than a certain proportion of volatile matter, or too large a proportion of volatile matter (when this is due to oxygenated compounds) the residue is of a non-coherent character, and is useless as a coke.

For a coal to give a good coke it must be sufficiently fusible under the influence of heat or give sufficient liquid products of not too volatile a nature at a low temperature to cause the particles of residue to adhere. We know that humus bodies do not fuse, nor does the carbon residuum formed by their degradation, whilst the resin bodies and hydrocarbons both fuse below 350° C. (482° F.) so that even from this it is a fair inference that the resin bodies and hydrocarbons derived from them are the coal compounds that condition the coking.

In a fine research made upon the coals of the Clyde basin, Carrick Anderson and Roberts showed that the coals of the upper seams, *i.e.* those of most recent formation, were non-coking, like the ell main and splint coal ; that at greater depth you obtain semi-coking coal, like the Drumgray coals ; whilst the lowest and therefore oldest seams are true coking coals, like the Haughrigg, Bannockburn main, and Kilsyth coals.

Taking now, the average composition of the coals of each class, ash- and moisture-free, we obtain :—

	Non-Coking. I.	Semi-Coking. II.	Coking. III.
Carbon . .	82·65	83·16	85·41
Hydrogen . .	5·55	5·48	5·36
Oxygen . .	10·10	8·98	7·22

The coking powers of these coals were then estimated by Campredon's sand test, and the averaged ratios are—

I.	II.	III.
3·9	4·4	13·5

We have seen that the outstanding difference between the humus and resin constituents of the coal bodies is that in the former there is a large excess of oxygen over hydrogen, whilst in the latter the hydrogen is at least equal to and sometimes higher than the oxygen. The composition of the three classes of coal shows clearly that the factor which has made the oldest coal a coking coal is the more complete degradation of the humus with elimination of oxygen, bringing the resin bodies and hydrocarbons up to a percentage which will supply enough luting material on decomposition to give a satisfactory coke.

As the hydrogen and oxygen in the resin bodies are nearly equal, if we deduct the percentage of hydrogen from the oxygen, the amount of surplus oxygen should give a rough indication of the ratio in quantity of the humus in these classes of coals, and on doing so we find :—

(1) 10·10 − 5·55 = 4·55
(2) 8·98 − 5·48 = 3·50
(3) 7·22 − 5·36 = 1·86

We see that as the surplus of oxygen increases the coking power falls, because the humus gets more and more in excess.

Anderson and Roberts made a large number of experiments with the coals to ascertain if possible the causes of coking in some coals and not in others, and they found, as we have

already seen, that with a feebly- or semi-coking coal, the coking property can be destroyed by treatment with caustic potash, and also by atmospheric oxidation at a slightly elevated temperature, but that with a strongly coking coal, although the coking property might be weakened, it was not destroyed. We have also seen that the effect of pyridine on a coal has the same result.

They also made the interesting observation that when these coals were heated to a temperature of 300° C. (572° F.) for three hours in an atmosphere of dry carbon dioxide, instead of gaining in weight as they did when heated in air to between 100° and 150° C. (212° and 302° F.), they lost in weight, and that the non-coking coals lost the most and the coking coals the least, that is, the humus bodies were even at this temperature beginning to decompose. The same experiment showed that after this treatment the percentage of coke was increased (probably fixed carbon is meant, as only three of the coals coked), and that in the feebly-coking coals the power of coking was entirely destroyed, but only impaired with the true coking coals.

From these observations the authors conclude that in all the coals resinoid bodies exist, which can be saponified by caustic potash, and which alone are accountable for the coking of semi-coking coals. In addition to these, in the true coking coal there is a constituent not so easily, if at all, acted upon by alkalies, oxidisable in air, but not volatile at 300° C. (572° F.).

They find also that the true coking coals melt in an atmosphere of carbon dioxide at 317° C. (603° F.), and this they take to be the melting point of the constituent referred to.

My own view is that this constituent is the hydrocarbons derived from the resin bodies, and that in a strongly coking coal they condition the coking after the unaltered resins have been oxidised or saponified.

If we make a proximate analysis of humus and of resin we find that the humus decomposes and leaves about 45 per cent. of fixed carbon, whilst the resin practically all distils off as gas and tar vapour, the hydrocarbons doing the same unless the heat is very high, in which case they also partially decompose to carbon, or at any rate their products do.

	Resin.	Humus.
Moisture . . .	0·69	2·59
Volatile matter .	97·97	51·71
Fixed carbon . .	0·81	44·67
Ash . . .	0·53	1·03
	100·00	100·00

When these coal substances decompose, the tar which distils from the humus bodies is a watery phenoloid tar which does not easily decompose, and as the heat slowly passes into the mass of carbonising coal distils forward in front of the rising temperature, and leaves behind but little pitch. The tar from the resin bodies is a rich oily tar, which also freely distils forward, but leaves enough pitch to have a distinct binding effect, whilst the hydrocarbons yield a heavy viscid tar that decomposes with deposition of pitch as the heat acts upon it, and is the strongest factor in the formation of coke.

The question now arises: At what temperature is coke formed? As is well known, the coalite process was based entirely on carbonising coal at 420° C. (800° F.). When heated at this temperature all coking coals yield a good, although not very hard coke, but the coke structure was completed, and beyond a slight hardening effect and driving out the remaining volatile matter, heating up another 550° C.(990° F.), had no physical effect upon it. Below 400° C. (752° F.), the residue was "tacky," that is, there was a little undecomposed tar left, so that 400° to 420° C. may be taken as the formation heat of coke.

Moreover, it is clear that at this temperature all the coal constituent that gives coking is destroyed, as if the low temperature coke is broken up and put back into the retort, and the heat raised to 1000° C. (1832° F.), no sign of any further adherence between the particles shows itself, and a broken up mass is drawn.

Messrs Burgess & Wheeler in their paper "On the Volatile Constituents of Coal," published in the *Journal of the Chemical Society* in April 1911, notice that between 700° and 800° C. (1292° and 1472° F.) there is an increase in the quantity of hydrogen yielded by the carbonisation of coal, and conclude that a compound exists in coal which decomposes rapidly at this temperature, yielding hydrogen alone (or possibly hydrogen and the oxides of carbon) as its gaseous decomposition product.

"Coal also contains a compound of less stability to the action of heat, which yields the paraffins as its gaseous decomposition products.

"Fractional distillation of coal in a vacuum confirms this view. It is possible by prolonged exhaustion at a low temperature to remove entirely the paraffin-yielding constituents, and leave behind a compound which decomposes at a higher temperature and yields hydrogen."

The "hydrogen-yielding constituent" they consider, is a degradation product of cellulose, and the "paraffin-yielding constituents," as most probably derived from the resins and gums originally contained in the sap of the coal plants, and these form the cement of a conglomerate of which the cellulose derivatives are the base.

I agree entirely with their last conclusion, and as long ago as 1890, in a paper on "The Spontaneous Ignition of Coal," read before the Institution of Naval Architects, defined coal as being formed "from the woody fibre and resinous constituents of a monster vegetation which flourished long before the earth was inhabited by man," but I quite disagree

with their theory that coal contains two types of compounds of different degrees of ease of decomposition, the one derived from the cellulose (which I have called "humus bodies"), decomposing only above the "critical period," of decomposition, which they define as between 750° and 800° C. (1382° and 1472° F.).

Apart from the evidence already adduced that cellulose itself and its immediate derivatives decompose at comparatively low temperatures, valuable evidence should be obtainable from the residue of coal that has been heated to temperatures below 750° C., as these will manifestly contain the bodies which decompose between 750° and 800° C.

We have seen that the coke body is formed below 450° C. (842° F.), that the compounds which give the luting material are already used up at that temperature, and that on powdering the mass and again carbonising at a high temperature, no further adhesion takes place between the particles, but it is found that the low temperature coke yields as large or an even larger volume of gas at temperatures between 450° and 1000° C. as it does below 450° C., that is to say, the compound left in the low temperature coke has very high gas-making properties. The composition of the gas so evolved is approximately :—

Hydrogen	71·13
Saturated hydrocarbons .	18·26
Unsaturated hydrocarbons .	0·52
Carbon monoxide . .	6·30
Carbon dioxide . . .	2·09
Nitrogen	1·70

And it is evident that the compound that yields this gas is that which Burgess and Wheeler consider a degradation product of cellulose.

If now we analyse low temperature coke, we find from its ultimate composition that, like the coal from which it was

made, it contains carbon, hydrogen, and oxygen, but that the ratio between these elements has undergone considerable alteration, decompositions of the primary products with formation of gas and tar having, as one might expect, reduced the percentage of hydrogen and oxygen in a greater ratio than it has the carbon.

If, as Burgess and Wheeler suppose, the action below this temperature has been an elimination of the resin bodies and a survival of the cellulose derivatives, which I have called "humus bodies," the ratio of hydrogen and oxygen remaining will clearly indicate this, as we have already seen that the marked characteristics of this class are high oxygen and low hydrogen. In the coal itself this has been to a certain extent masked by the resin bodies, the characteristics of which are that the hydrogen is if anything in excess of the oxygen, and these having been eliminated, there would be nothing to cloak the evidence of the preponderance of oxygen, which in the earlier primary reactions would have been eliminated in smaller proportions than the hydrogen.

Selecting a coal high in oxygen as being most likely to contain a large proportion of the cellulose derivatives, its composition before and after carbonisation at 450° C. is given below :—

	Original Coal.	Residue after Carbonisation at 450° C. (842° F.)
Carbon	81·93	87·33
Hydrogen . . .	4·86	3·89
Oxygen	10·95	6·91
Nitrogen . . .	1·06	0·69
Sulphur	1·20	1·18

This certainly shows no concentration of oxygen, but, as one would expect, a decrease in comparison to the hydrogen.

A second coal lower in oxygen was then taken, and

carbonised at the same temperature as before, the result being :—

	Original Coal.	Residue after Carbonisation at 450° C. (842° F.)
Carbon	85·56	87·59
Hydrogen . . .	5·00	4·06
Oxygen	7·11	6·02
Nitrogen . . .	0·98	1·06
Sulphur	1·35	1·27

So that here, again, more oxygen than hydrogen was eliminated.

Bornstein also made a long series of experiments on the composition of coal, and the residues after distillation at 450° C., which show results of the same character, and make it perfectly clear that no selective destruction of the resinoid bodies and survival of the cellulose derivatives has taken place.

The question now arises as to what is the nature of the luting material which, agglomerating the residual carbon into coke below 450° C., is yet capable of producing large volumes of gas at higher temperatures, and at the same time becomes harder and stronger.

Most observers look upon the luting body in the coke as tar residues left behind as the slowly advancing heat distils the more volatile portions of the tar formed by primary actions. Others, like Wedding, consider it as carbon deposited by the breaking down of hydrocarbon gases owing to contact with the red-hot surface of the carbon, and as a proof of this adduce the formation of the so-called " coke hairs " found in crevices in the coke, supposing that they are produced by the streams of rich hydrocarbon gas, such as ethane and ethylene, leaving the coal, and in the heat of the retort decomposing with separation of carbon, these coke

hairs consisting of fine tubes of graphitic carbon, which branching out in every direction bind adjoining masses together. This theory is, of course, untenable in view of the fact that coke is formed at a temperature far below that necessary to yield graphitic carbon, an action taking place only above 900° C. (1652° F.), with diluted hydrocarbon gases.

Lugi, Donath, and their followers hold that it is a molecular alteration in the carbon molecule ; but although many actions take place with carbon and its compounds that are not clearly understood, it is unnecessary in the present case to rely on any such complicated explanation.

My own view, and one which I think can be proved abundantly, is that when a charge of coal is put into the red-hot retort or oven, the layers in immediate contact with the walls are heated up and almost immediately decomposed with the rush of steam and smoke we know so well. The lid or door is shut, and carbonisation proceeds as the heat slowly penetrates into the mass, and even an inch away from the hot walls the temperature rises only very gradually. The first action of the heat is to drive off " pit water," *i.e.* the moisture which the coal has acquired from rain or washing at about 200° C. (382° F.). The " hygroscopic water," *i.e.* that which is constitutional, comes off, and the humus bodies begin to decompose and give also as their first product water. All the water vapour formed from these actions distils forward into the first layer cool enough to condense it, so that even with a charge of what one would consider dry coal, if the retort be opened half an hour after charging, the centre of the mass is found soaked with water, whilst in a coke oven in which the charge is wet freshly washed coal, it will be streaming with water.

As the temperature rises to 300°–350° C., the coal becomes semi-fluid, decomposition of all the coal bodies commences and rapidly increases in vigour with each accession of heat, and the fluid tar from the humus, the slightly viscid tar

from the resinoid bodies, and the rich heavy tar from the hydrocarbon gases, go forward as vapour with the gases, away from the heat and seeking the cool zones. It must be remembered that, as the heat spreads to the zone in which the water has condensed, this again evaporates and renders a large amount of heat latent, so cooling it down and leading to the condensation of the tar vapour, and when in turn this is reached by the advancing temperature and is heated to 350°–400° C., it is only the more volatile portions that distil again, and a deposit of pitch is left which binds the half-coked coal, whilst as the temperature rises above 700° C. the residues in the semi-coke and pitch further decompose until the hard coke is left, which consists of little else than carbon, ash, and traces of hydrogen and oxygen, either combined still or occluded by the coal.

It may be objected that if this is the only cause of coking, then the layer first heated next the wall of the retort, having no tar condensed on it to redistil with deposition of pitch, might be expected to be of inferior character and of a friable nature, whilst perhaps it is the best layer of coke in the oven. The explanation of this is that, although the distilling and redistilling into the cool zones of the charge is the main action taking place, yet each individual lump of coal is being affected in much the same way as regards the passage of heat. The heat must pass into the centre of each lump before carbonisation is completed, and as it is conducted only slowly, the exterior of the lump is at a high temperature before the centre has finished distilling tar vapour, and this passing through the hot exterior is decomposed with deposition of pitch.

It is clear that the tar which is least volatile and leaves the largest residue of pitch will be the one that is most valuable in inducing coking, and on completed carbonisation giving the strongest coke ; and it is the heavy hydrocarbon tar that does this, whilst the oil from the resin distils so

easily that it is a far more important factor in the volume of tar than in the coke, whilst the humus tar only helps the general action.

If, however, the distillation out of the mass could be prevented all the tars would help in the coking, and the flaming coals, like some of the South Staffordshire non-coking coals, could easily be made to coke. This may be done by rapid heating, and there are plenty of semi-coking coals in the country which, if carbonised rapidly so as to give no time for the redistillation of the resinoid tar before the temperature of decomposition is reached, make a good coke, whilst distillation under pressure would tend to do the same thing.

It must be remembered that a semi-coking coal will give much better coke when carbonised in a gas retort than in a coke oven, as in the latter the slow advance of the heat gives ample time for the redistillation of the tar. The same thing is seen if you try to carbonise smalls from, say, a South Staffordshire coal under these conditions. The heat gets rapidly through each particle of coal and the tar distils away, and the residue does not coke ; but if you take it in large lumps, the outside of the mass gets red hot before the inside distils, and the tar vapours and hydrocarbons decomposed by the hot crust give an excellent coke.

No matter how high the temperature is pushed during the carbonisation of coal, the coke will always contain some volatile matter, probably gases occluded in minute pores and cavities in the coke substance. John Parry in 1872 made a large number of experiments with various samples of coke, some by simply heating to as high a temperature as could be attained under ordinary conditions in a gas furnace, and also when heated in a vacuum, and found that these gases so held, instead of being simply air absorbed on cooling as had been supposed, consisted of gases of the same character as those evolved during the last stages of coking.

A gas coke with which he tried one experiment gave on analysis :—

Carbon		84·360
Hydrogen		0·187
Oxygen	}	6·303
Nitrogen	}	
Sulphur		0·850
Ash		8·300

The oxygen and nitrogen, which are determined as usual by difference, were so palpably wrong that the coke was heated for 7·55 hours to as high a temperature as possible, and then gave on analysis :—

Carbon		89·450
Hydrogen		trace
Oxygen	}	1·305
Nitrogen	}	
Sulphur		0·795
Ash		8·450

Twenty grams of the coke were then heated in a vacuum, produced by a Sprengel pump, and in $2\frac{1}{2}$ hours yielded 361·5 cc. of gas containing :—

Carbon dioxide	22·8
Carbon monoxide	13·4
Hydrogen	50·0
Methane	13·8

and also water and tarry matter. On continuing the heating for $14\frac{1}{2}$ hours altogether 1117·2 cc. of gas were obtained, but in the latter portions they consisted of oxides of carbon and hydrogen only, whilst in the last hour nitrogen made its appearance, and the analysis of the gas was :—

Carbon dioxide . .	9·385
Carbon monoxide .	8·200
Hydrogen . . .	81·200
Nitrogen . . .	1·215

This gives a good idea of the difficulty of freeing the coke from the last traces of gas, and it is doubtful whether it could be got entirely free.

It is probable also that some of the gas obtained is present in combination in highly resistant bodies of the same character as the hard pitch that forms the binding material in low temperature coke. Even the coke hairs formed during coking from the decomposition of hydrocarbon gases have been found to consist of :—

Carbon . . .	95·729
Hydrogen . . .	0·384
Oxygen . . .	3·887

Many experiments have been made on these residual traces, and it seems probable that they are due partly to occluded gases, partly to carbonaceous residues, and partly to traces of hydrocarbons retained in the pores of the coke.

It is often stated that the ash of coal and its derivative coke represents the mineral and inorganic matter absorbed from the soil during the growth of the vegetation from which the coal was formed. Although this is probably partly true, a consideration of the composition of the ash of coal at once shows that this was not entirely formed from plant life, as alumina, which is rarely present in the ash from wood and vegetation, is one of the most important constituents of the coal ash, as may be seen from the following table of analysis, which is due to Muck :—

Ash.	Westphalian Coal.	Lower Silesian Coal.	Dowlais Coal.	Anthracite from U.S.A.
	Per cent.	Per cent.	Per cent.	Per cent.
Silicic Acid . .	27·365	31·300	35·730	53·600
Alumina . . .	22·552	8·310	41·110	36·690
Oxide of Iron . .	46·900	54·470	11·150	5·590
Lime . . .	2·686	3·440	2·750	2·860
Magnesia . . .	·000	1·600	2·650	1·080
Potash . . .	0·300	0·070	not estim.	not estim.
Soda . . .	0·237	0·290	not estim.	not estim.
Sulphuric Acid .	traces	0·520	0·290	0 ?
Phosphoric Acid .	0·541	not estim.	2·000	0 ?

Moreover, it is perfectly clear from the method of formation of many of the drifted deposits that have been converted into coal, the earth disturbances and the covering of the deposits by mud, silt, and sand, that mineral matters other than those due to plant life must find their way into the coal. When coal is converted into coke, as the latter represents only 62 to 80 per cent. of the weight of coal, and contains all the ash, it follows that the ash in coke is higher in proportion than in coal. Coal contains from 1 per cent. of ash in some Welsh coals up to 20 per cent. in some cannel coal, and when stress is laid upon the purity of the coke a coal must be selected with as low a percentage of ash as is commercially possible.

The changes which take place in the nature of the mineral matter of the ash during carbonisation are not of a very important character. The carbonates of the alkaline earths are converted into oxides, carbon dioxide being evolved, and these oxides will then sometimes combine with silica to form silicates. Sulphur, which is one of the most deleterious compounds in coke for metallurgical use, is sometimes volatilised to a small extent during coking, and water of hydration may be driven off from the silicate of alumina.

The theory has been advanced that the silica present in coal, or part of it, is in the form of organic silicon compounds derived from the vegetation, and that on coking the coal these play an important part in hardening the coke. The

basis of this idea seems to be that when carbon is embedded in a mixture of sand and coke, and is heated to a temperature between 1600° and 1900° C. (2912° and 3452° F.) it undergoes a complete change and acquires the hardness and metallic ring of a good metallurgical coke, and also its silvery appearance, but inasmuch as no such temperature could be employed in practice, and as experiments have shown no sign of the formation of carborundum or ferro-silicon in coke, the idea does not seem a very likely one.

Coke varies very much, not only in its chemical and physical characteristics, but also in external appearance. It may generally be accepted that with the same kind of coal the higher the temperature, and the longer the exposure of the coke to it, the harder, more dense, and less easily combustible will it be, whilst the appearance is largely conditioned by the method of carbonisation.

In the beehive oven, where most of the heating is from the top, the escaping gases from the carbonising coal have to pass upwards through the whole mass of red-hot coke above, contact with which decomposes the hydrocarbons and deposits the carbon in almost metallic-looking films throughout the mass. This gives the bright light grey surface that used to be so highly prized in the old beehive coke. On the other hand, if the gases are drawn away so as to prevent as far as possible excess of surface contact and pressure, this silvery appearance is not produced, and the coke looks black and dead, as is seen in gas coke, and also to a less extent in recovery oven coke.

Some observers claim that this deposition in bright films is characteristic of the decomposition of methane, and is given only by this particular gas, but the difference in the form of the deposited carbon is due to whether it has been decomposed by radiant heat or contact heat. If an easily decomposed hydrocarbon like acetylene is heated by passing between the walls of a very highly heated tube placed

vertically to lessen contact as far as possible, the radiant heat is sufficient to decompose it, and the carbon is deposited as a cloud, but where the hydrocarbon is more resistant and comes in actual contact with the heated surface, then the carbon is deposited in a dense form as a film of great density, which in time builds up masses of retort carbon. It is only when the film is very thin that the bright appearance is produced.

The duller surface of the recovery oven coke gave rise to great prejudice against it in the minds of the iron smelters when recovery plant was first introduced, but this was probably caused by the fact that until the recovery plant was perfected—the heat being applied from outside the oven instead of the inside, as with beehive ovens—the coke was not so thoroughly carbonised, was softer, and too easily attacked by the carbon dioxide in the blast furnace, and so not so strong or so economical in practice.

In most oven carbonisation the face of the coke nearest the hot wall of the furnace shows a curious undulated surface consisting of discs, six to eight inches in diameter, and higher at the centre than at the periphery—these are generally known as " cauliflower heads " by the coke burners—and crevices of cleavage run into the mass from the lowest point to the area which was last heated to the full temperature in the carbonising process. So regular are these appearances, and so like the columnar structure found in some formations, that they have sometimes been spoken of as if they represented a form of crystallisation, which is, of course, wrong.

They appear to be formed from the escape of gases, which causes the whole mass to swell. After the first few hours this ceases, and a general contraction of the whole body takes place, which, being fairly even in every direction, fissures the coke in circular masses. If the coke is drawn when the volatile matter just ceases to come off, the heads are not found, but the crevices are there. The coke, however, is left heated to its highest temperature for a considerable

period to harden it, and this causes further shrinkage, which, taking place mostly where the crevices have been formed, owing to the heat entering the mass most easily at these points, leaves the central portion between the cracks standing up a fraction of an inch above the densest parts.

Near the doors of the oven, black dull-looking masses of coke are often found, resembling gas coke, and known as "black heads." These are formed by the coke at this point not being sufficiently heated to complete properly the carbonisation.

As a rule, it is found that the higher the temperature at which the oven has been worked, the more thorough has been the decomposition of the hydrocarbon gases, and vapours passing through the red-hot coke and the carbon so deposited increase the yield. High temperature and long exposure to the heat after carbonisation is finished also render the coke harder, denser, and less easily ignited.

The composition of the coal has so great an influence on the yield of coke that any comparisons of the percentage yield by the various forms of oven, are bound to be misleading; but the alterations from the earlier forms of oven to the modern oven may be taken as representing a 10 to 12 per cent. greater yield of coke.

The idea of converting coal into coke first arose from the desire to supplement charcoal for metallurgical work by some other form of fuel which would have much the same characteristics, this being necessitated by the fact that the timber on which the charcoal supply was dependent was rapidly becoming depleted. The characteristics desired were local intensity of combustion, strength of structure, smokeless burning and infusibility, together with as small a proportion of sulphur as possible. The only raw coals which could have been employed to fulfil these requirements were splint coal and anthracite, which latter has always been comparatively high in price, and somewhat difficult to deal with in practice.

The bituminous coals, which were the ones generally available, could not have been used in the blast furnace, on account of their swelling, softening, and forming arches, which would have interfered with the descent of the charge in the furnace and passage of the hot gases, whilst the intensity of the heat would have been low, owing to the amount withdrawn by the gases and vapours, and rendered latent in distilling off these volatile products, and also because of the oxygen present in the coal. When, however, bituminous coal is converted into coke the residue is infusible, its friability is decreased, and with the concentration of the carbon, although the total increase in calorific value is small, no heat being withdrawn by the distillation, the local temperature is very largely augmented.

With the increase in coal mining which took place in the first half of the last century, another important reason for the coking of coal presented itself. In all collieries raising bituminous coal, the percentage of slack and small was high. Where any of the coal is of younger formation, the smalls will sometimes amount to 40 to 50 per cent., and as before the introduction of automatic stoking machinery the demand for this was very limited, all the screenings and smalls of a colliery had to be sold at a very low and unremunerative rate. With a comparatively small amount of labour, however, these screenings could be converted in the old coke meilers and beehive ovens into larger masses of hard coke exactly suited for metallurgical and furnace work.

Another reason, which was not at first recognised, but has now assumed great importance, is that the sulphur present as pyrites and other sulphur compounds in all coal can be substantially reduced at a very low cost in properly made coke. The larger pieces of pyrites having been hand-picked, a considerable proportion of the impurities, including residual pyrites, can be got rid of by crushing the coal and washing it, when being heavier than coal, the pyrites can to a great extent

be separated by gravity in the trough and jigger washers. On coking the washed coal the long exposure to heat expels a considerable proportion of the remaining sulphur, which comes off with the gases as sulphuretted hydrogen, carbon disulphide, and other organic compounds of sulphur. Quenching the red-hot coke on its removal from the oven eliminates another small percentage, so that a very substantial decrease in this deleterious constituent of coke for metallurgical work can be obtained.

With the introduction and general adoption of coal gas in the early years of the last century, coke was yielded as a by-product of the destructive distillation, but the gas manufacturers, looking upon it as a by-product, have from that day down to the past few years paid little or no attention to modifying the process of gas manufacture with a view to improving the quality of the coke produced ; with the result that gas coke has always been looked upon as an inferior product, and the market which it commanded has been of a limited character. It has never achieved much success as a domestic fuel, and its chief output has been due to its use by small manufacturers, for horticultural work, heat production in the gasworks, and the generation of water gas and producer gas.

Coke may be divided into two main classes ;—

(1) Metallurgical coke and furnace coke, made by processes in which everything has been done to obtain the largest yield of coke having definite characteristics, and in which the by-products, gas, and tar are either disregarded, or considered of secondary importance.

(2) Gas coke, made by processes designed to give the largest yield of gas, in which as much of the carbon as possible shall be in gaseous combination, the coke residue and tar being looked upon as of secondary importance.

In making the first class of cokes, the factors which are desired in the process are—using coal only rich enough in

resinic volatile matter to give the necessary coking or binding properties to the mass ; to crush the coal to uniform size ; to use large charges densely packed ; and to carbonise for long periods, raising the outer crust of coke first formed to as high a temperature as possible, so that, as the heat penetrates into the mass, the hydrocarbon gases and tar vapours being evolved shall be decomposed by contact in their passage through the envelope of red-hot carbon, depositing as much of the gasified carbon as possible, so that it is only the more stable hydrocarbon gases and most volatile vapours that escape ; the ideal carbonisation from the coke-maker's point of view being the retention of the whole of the carbon in the mass.

In gas manufacture, on the other hand, in the ordinary process employed at over 90 per cent of gasworks, the coal used is as rich in resinic volatile matter as can be obtained without going to undue expense. Small charges are used in order to reduce the time needed for carbonisation, and also to reduce the contact of the gas with too large a surface of hot coke, and the temperature employed is limited only by its effect on the life of the refractory material used, and to avoid stopped ascension pipes and other troubles inseparable from overheating, and to continue the carbonisation only long enough to drive out all volatile matter. Under these conditions the gas yield is increased to the highest limits compatible with leaving in it enough hydrocarbon gases to comply with parliamentary requirements as to illuminating and heating value, and the coke is looked upon as a by-product that will pay a share of the coal bill. The ideal condition of carbonisation from the gas manager's point of view is the conversion of the whole of the coal into gas, an ideal within measurable distance when using high heats obtained by employing 15 per cent. of the coke for heating the settings and converting the remainder into water gas.

It will not be out of place at this point to discuss a matter

which I feel very strongly upon, and that is the use of coke as a domestic fuel, and the influence this has upon the future of the gas industry, and also upon the efforts of the various smoke abatement societies to cleanse our town atmospheres.

The whole question of fuel economy is so closely allied to the problem of smoke prevention that it is impossible to consider the one without alluding to the other, and if only sufficiently drastic steps were taken to enforce rational methods of domestic heating, both economy of fuel and cleansing of the atmosphere would follow.

In the south of England, at any rate, the domestic grate using bituminous coal is the principal cause of the smoke cloud which, hanging over the big towns, cuts off the direct rays of the sun, ruins health, shortens life, kills vegetation, and begrimes and finally helps to destroy our public buildings. Further north in the manufacturing districts, the factory shafts, in spite of restrictive legislation and mechanical improvements in stoking, do even more towards polluting the atmosphere.

Many estimates of the relative amount of pollution due to manufacturing works and domestic fuel have been made, but as the question of what is the ratio of smoke production from the various sources that pollute the air varies enormously with the locality, no very satisfactory conclusion has been arrived at. If you take London, Dr Shaw's estimate that 70 per cent. of the smoke is domestic would probably be about correct, but if you collected your statistics in Sheffield or Birmingham, the figures would most likely be reversed. There is one thing certain, however, and that is that domestic smoke is produced throughout the whole length and breadth of the land, whilst the factory shaft concentrates its attention on the more limited area of the manufacturing districts.

Although the smoke from the domestic chimney has been

execrated for the part it has played in the pollution of the atmosphere from the earliest years of the fourteenth century down to the present day, it is surprising how crude the ideas are that exist as to its composition and the method of its production. In the open fire, the radiant heat given by the incandescent fuel is the heating agent, and although undoubtedly wasteful in fuel, owing to the largest proportion of the heat escaping with the products of complete and incomplete combustion up the chimney, still it is so far more hygienic and more comfortable than any other method of heating, that one would be sorry to see its place taken by any other form of heat production, in spite of the economic advantages of central heating systems or slow combustion stoves.

With the ordinary grate, using bituminous coal, the production of smoke means waste of fuel, but great as this is in the aggregate, it is small as compared with the other losses due to actions taking place in the fire itself, and loss of heat escaping up the chimney. When bituminous coal is fed on to the burning fire the action which takes place on the newly added portion is practically the same as that occurring during the distillation of coal. It is during this period that a very large proportion of the heat units in the coal are lost, owing to the amount taken up in decomposing the coal and converting the volatile portions into vapours and gases. During this period the coal, heated by the fire from below and comparatively cool above, distils off tar vapours, coal gas, and steam in proportions which vary with the temperature. In the early stages, the surface of the fuel being too cool to lead to their ignition, these products escape as vapours up the chimney, mingled with anything from eight to thirty thousand cubic feet of air per hour, according to the draught in the chimney. In an ordinary flue an analysis of the escaping products would give an approximation to the following :—

Carbon dioxide . .	0·70
Methane . . .	0·36
Hydrogen . . .	0·29
Carbon monoxide .	0·01
Oxygen . . .	19·85
Nitrogen . . .	78·79

And these gases together with water vapour escape up the chimney.

During this period of smoke production no soot is formed. The physical properties of the cloud of vapour provide an interesting study, as it explains one of the secrets of the lasting power of smoke, and the way in which it acts. A most beautiful and instructive experiment shows to perfection the structure of smoke as it escapes from a burning object. A puff of smoke blown through a small glass cell illuminated from below by oxy-hydrogen or arc light, and examined under a low-power microscope, reveals the fact that it consists of excessively minute vesicles, which are in a marvellous condition of motion, and which will remain floating in the stream of air or gas until impact with a solid surface causes a bursting of the little liquid envelope, forming a microscopic drop of tar on the solid against which it has struck, and liberating the contained gases.

This period is the one in which the most serious waste takes place, as not only is the greatest amount of heat being rendered latent by the distillation out of the coal of these products, but they also escape unburnt up the chimney. After a period, which varies in length according to the amount of coal which has been fed on to the fire, sufficient heat finds its way to the top of the fuel to ignite some of the escaping vapours, and the bright illuminating flame is then formed above the surface of the fire. This flame radiating a considerable amount of heat, owing to the incandescent particles within it, the waste ceases to be as great as before; but a

large amount of vapour will be noticed to be escaping still unburnt, owing to some of the hydrocarbons being so diluted with steam, and the cold air sucked in over the surface of the fire as to stop their combustion.

If now the flames themselves be watched it will be seen that they become red and lurid towards the top, and are emitting particles of carbon. It is during this period of combustion that soot is deposited in the chimney and appears in quantity in the smoke, which now consists of tar vapour, soot, water vapour, products of combustion, and excess of air, together with the residual nitrogen from that portion of the air which has been used in the combustion, and also particles of ash sucked up by the draught in the chimney.

As time passes on the fire burns clear, the amount of flame becoming extremely small and consisting chiefly of carbon monoxide, and practically smokeless combustion is attained. Until more coal is fed on no further pollution of the atmosphere takes place, whilst the clear fire radiating out the heat given by the combustion of the incandescent carbon is doing more heating work than at any other period.

In order to overcome the trouble of smoke whilst using solid fuel many forms of grate have been suggested, the most successful of them being dependent upon the principle of feeding fresh fuel to the bottom of the fire instead of to the top, so that as the tar, hydrocarbon vapours, and steam distil out from the coal, they have to pass through a mass of incandescent carbon above, which decomposes the complex tar vapours into simple hydrocarbons. These are then completely burnt up on reaching the fresh air supply at the top of the fuel.

The fact, however, that any special form of grate would require the removal of the old type and introduction of the new, has been sufficient to prevent any success in this direction, and what is really needed to make smoke prevention a practical possibility is the introduction of a fuel which could

in every way be treated like coal, which would be as easy to ignite, would burn with a cheerful flame, and would in reality commence its combustion just at that period when, in a fire, the smoke has ceased and the fire has burnt clear.

I have always been strongly of opinion that the only way in which the smoke problem could be solved was in stopping the direct combustion of bituminous coal in grates and furnaces, and employing the gasworks of the country to convert the coal into gaseous and solid fuel, both of which would give us smokeless combustion, at the same time extracting in useful form those volatile products which, in the manufacture of gas yield tar and ammonia salts, but in the stove or furnace form smoke.

The domestic use of gas for heating purposes has advanced with great rapidity. Although at first sight its cost appears to be considerably higher than that of coal, yet when used under proper conditions it is practically not much more expensive, the economy in handling and cleanliness making up for most of its extra cost. In a very large number of households at the present time gas is employed for cooking, and for heating the bedrooms, whilst it is only in the sitting rooms that solid fuel plays an important part. Coke, on the other hand, owing partly to prejudice and partly to the fact that it is difficult to ignite, and burns freely only when the stove happens to have a good chimney draught to aid it, has never proved a serious rival to coal.

As we have seen, when coal is burnt upon the domestic fire a process of distillation, very much akin to that which took place in the old meiler heap, is set up, and continues until the heat has penetrated the mass sufficiently to ignite the gas distilling from the top of the coal, and this portion of the fire, being cooled by the rush of air over its surface induced by the chimney draught, often allows two-thirds to three-quarters of the gases and vapours from the freshly fed on coal to escape up the chimney unburnt before it

ignites, and by the radiant heat of the carbon particles in the flame adds to the heat from the incandescent carbon in the lower portion of the fire.

A pound of bituminous coal may be taken as containing in round numbers 14,000 B.Th.U., and the distribution of this in a fire which has just been fed with coal may be taken as follows :—

In Gas—5 cubic feet at 570 B.Th.U.	2850	Lost 81 per cent.
,, Tar—·05 lb. at 15200 B.Th.U.	760	
,, Moisture	250	
,, Decomposition and volatilisation	1200	
,, Products of combustion	6000	
,, Grate and ashes	265	
,, Radiant heat from coke	2485	Used 19 ,, ,,
,, Radiant heat from flame	190	
	14,000	

So that the heat utilised in the room amounts to less than one-fifth of the heat that is in the coal.

When, however, coke is used the loss due to the first four sources has already taken place in the conversion of the coal into coke either at the gasworks or in the oven, and the amount of heat utilised as radiant heat in the room is nearly three times as great ; but unfortunately the prejudice against gas coke as a domestic fuel that has been created in the public mind has to a great extent limited its use.

If you attempt to impress upon any one the value of coke as a fuel, and the importance from a hygienic point of view of using a smokeless fuel, the reply is in most cases that coke gives a dull cheerless fire, and that the fumes from it are so full of sulphur, that the slightest back draught nearly chokes every one in the room. There is a solid basis of truth in these objections. Unless there is a more than usually strong draught in the chimney the high temperature coke of the

present day does not burn satisfactorily, and, to the householder accustomed to a cheerful flaming fire, appears dull and depressing, whilst the sulphur fumes, if they escape into the room, are undoubtedly unpleasant, although useful as a warning, as under the same conditions carbon monoxide is also probably present and will give a headache, if no worse results.

All this, however, is caused by the high igniting point of the coke, which makes it difficult to light the fire, and also slows down the combustion so that without a strong draught you never get a bright fire. The igniting points of coal and of coke are dependent entirely upon the amount of volatile matter the fuels contain; an anthracite, which is the nearest approach to carbon found amongst the coals, needs a very high temperature to ignite it and a strong draught to keep it burning, whilst a flaming coal with its 32 to 40 per cent. of volatile matter can be ignited readily by a few burning sticks in a heap on the ground, and burns away rapidly with a strong blazing combustion.

A high temperature coke contains only traces of volatile matter, so held that a temperature far above that yielded by the paper and wood used to ignite the fire would be required to drive it out, so that its igniting point is about that of carbon—*i.e.* nearly double that of a bituminous coal or a low temperature coke, which is about 520° C. (968° F.). This gives the latter the ease of ignition and free burning necessary to make a bright fire, whilst the escape of the combustible volatile matter gives a cheerful but non-luminous flame.

The limit of volume in gas-making, if not already reached, is fast being approached; economies are day by day getting more difficult to make; and coal is not likely to cheapen. All this means that the chance of considerable reduction in the price of gas is getting less and less. If the price of gas could be reduced in our large cities to the price charged at Widnes the consumption of gas could be economically increased, and

for power and heat gas would hold an unassailable position ; but this can never be done under existing circumstances, because, even if the gas could be made at the necessary price, the increased output of coke would exceed the demand. If only, however, the companies would live up to their title of " Gas, Light, and Coke Companies," and bestow as much care on the coke as on the gas, and cater for the supply of a good domestic fuel at the price of coal, instead of treating coke as a by-product, the demand for it would soon reach a point that would enable the desired reductions in the price of gas to be made.

There is no need to fear as to the other by-products ; the output of sulphate of ammonia could be doubled without affecting the market, and a good tar will look after itself. It was high heats that ruined the tar market, and with the demand for tar increasing for road work, no flooding of the market need be feared.

During the last few years the statement has several times been put forward that " as the gas manager's end and aim is gas, it is his duty to obtain the greatest volume possible per ton of coal," but with this I venture to disagree. The gas manager's duty is to obtain the greatest possible value per ton of coal, and until every industry dealing with coal recognises that in this respect their end is the same, little economy will be possible in our rapidly diminishing store of coal.

The pressing of temperatures in carbonisation to higher and higher degrees with the old conditions of lightly charged retorts has given larger yields of gas, but it has loaded the gas with carbon bisulphide, depreciated the coke, and ruined the tar.

One of the chief claims for the adoption of the full charge horizontals and intermittent vertical retorts for carbonisation is that they have improved the character of both coke and tar. As has been shown, this is due to a certain proportion

of the gas and tar vapour coming off through the cool core, and so escaping over-cracking ; but it can be only a partial improvement, whilst, as far as the coke goes, the nearer it approaches metallurgical coke the less it is fitted for domestic fuel. True it is that where the coke has been made harder and brighter the gas manager's market has improved, but it has been in its use for furnaces, manufacturing processes, and for producers, that the increased demand has been felt and not for domestic use.

Even for the heating of the furnaces the coke made at extreme temperatures is not as good as when the heats were slightly lower, and in Germany this is beginning to be realised. Korting, in a paper read in 1911, points out that the inclined settings, which used to work with 12 per cent, of fuel, now required fully 16 per cent., an increase due partly to higher temperatures, but largely to more highly carbonised coke.

Already the strides forward which gas has made as a domestic fuel are telling the tale in our atmosphere, and the yellow fogs of the last century are getting rarer, and if coke could be made a domestic fuel by leaving in it 6 to 8 per cent. of volatile matter, to facilitate ignition and give a flame, the gasworks of the country could command the fuel market.

The sale of gas cannot be pushed beyond a certain point without overstocking with coke. The sale of both *pro rata* must be pushed ; and if only the gas manager could be persuaded that this is the right road, he would be backed up by the smoke reformers and the public, and find himself able to sell a fuel coke at the price of the best coal.

Col. Scott-Moncrieff suggested many years ago the use of a half-coked coal as a fuel supply, and tried to make a commercial article by carbonising coal at the ordinary gas-retort temperature, drawing the charge when half the usual volume of gas had been distilled out from it. Two factors, however, led to failure, the one being that the time was not ripe, and the second that the means by which he proposed to

carry out his entirely admirable idea could never give a uniform fuel.

The idea, however, was revived in 1907 by Mr W. Parker, who found that by using a temperature of 420° C. (800° F.) with iron retorts, the whole of a charge of coal could be converted into a low temperature coke, uniform in composition, and containing from 8 to 14 per cent. of volatile matter, and which was an ideal smokeless fuel. This was christened "Coalite," and the material was made in thick cast iron tubes, which were heated to between 450° C. (843° F.) and 500° C. (932° F.). The diameter of the tubes tapered from $4\frac{1}{2}$ inches at the top to $5\frac{1}{4}$ inches at the bottom, the length being 10 feet, and twelve tubes were cast together into a block approximating to 2 ft. 6 in. by 1 foot. These were fixed vertically in the setting, which consisted of twenty-four to thirty-two batches of tubes to the bench. The retorts or bunches of tubes were fitted with a door at the bottom for the removal of the "Coalite," and a chamber at the top connected by a pipe to the Cort anti-dip hydraulic main.

The coal was fed in by gravity from above, and was carbonised for four hours, at the end of which period two-thirds of the volatile matter had been distilled off, and the charge had shrunk sufficiently to be easily discharged when the bottom door was opened. The temperature in the coal varied usually from 450° C. (843° F.) in contact with the skin of the retort to 420° C. (800° F.) in the centre of the charge, and the products were treated in accordance with the usual gasworks practice.

In such a bench of retorts forty-eight tons of coal were carbonised easily in the twenty-four hours, and if the bottom doors were tight a ton of ordinary gas coal as nuts would yield 5000 cubic feet of 19 candle gas. If, however, the central core of the charge became choked with tar too early in the distillation, a back presure was thrown on the bottom doors, and leakage lessened the yield.

It is unwise to use a coal with too high a percentage of volatile matter, owing to trouble from swelling and frothing in the tubes, but this applies only to certain coals. Good results were obtained from a coal the analysis of which gave :—

Moisture . . .	2·98
Volatile matter . .	33·16
Fixed carbon . .	61·08
Ash	2·78

The low ash is, of course, a great advantage.

The coalite yielded by distilling forty-eight tons a day amounted to thirty-four tons, six of which were breeze, the whole being equal to 70 per cent. of the coal used. On analysis it gave the composition (dry) :—

Volatile matter . .	10·43
Fixed carbon . .	86·13
Ash	3·44

For various reasons, none of which were connected with the fuel itself, so far coalite has not proved a commercial success ; but it has convinced everyone who has used it that it is infinitely superior as a fuel to any bituminous coal, and has created such a demand for a smokeless fuel that some imitations, which differ from gas coke only in name, have been able to find a market.

The best known of these is " Coalexld " made by mixing a very small proportion of alkaline nitrates with the coal before carbonisation. These evolving small traces of oxygen on their decomposition give small areas of high temperature during destructive distillation, and so give a slight increase in the gas yield.

Another is made by cooling the hot coke when it is drawn from the retort by smothering it with a layer of coke breeze,

instead of quenching it by water in the usual way, and is known as "Charco."

Through the kindness of Mr Alexander Wilson I obtained specimens of coke, Coalexld, and "Charco," all made at Glasgow from the same coal, which on analysis gave the following results :—

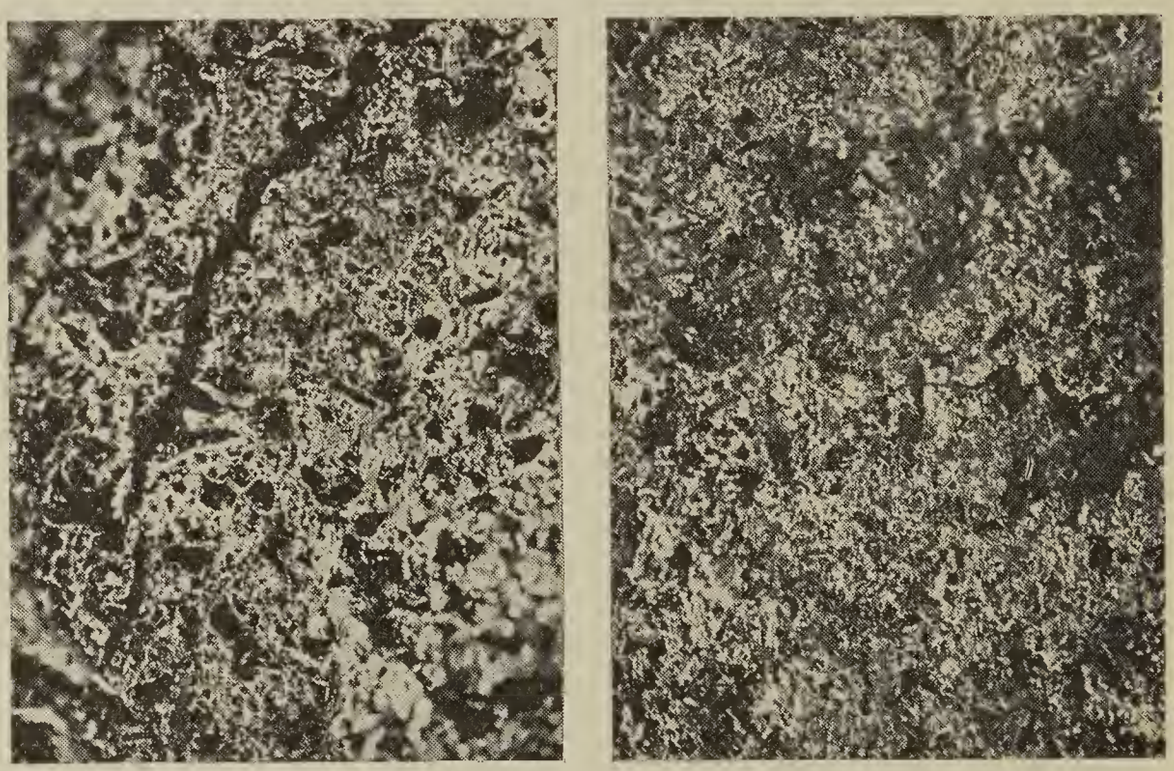
	Coke.	Coalexld.	Charco.
Moisture after air-drying . .	1·83	1·08	0·83
Proximate analysis (on dry)			
Volatile matter . . .	4·37	3·13	2·66
Ash	5·98	5·86	5·43
Sulphur	0·48	0·43	0·40
Calorific value (calories) . .	7765	7651	7615
Calorific value B.Th.U. . .	..	..	..

And as the "smokeless fuels" contain rather less volatile matter than the coke, it is hard to see how they can be better domestic fuels.

A factor of great importance in fuel to be used for manufacturing purposes is constancy in heating value, as any wide variations in the temperature obtained by its use may seriously affect a process. In this respect coke is an ideal fuel, as Constam and Kolbe have shown that the combustible matter of all cokes produced under similar conditions has a constant calorific value of 14,400 B.Th.U. per lb., and that its calorific value may be determined by deducting ash and moisture and multiplying the residue by 14,400. This is approximately true for oven-carbonised coke, but does not hold good with low temperature coke.

In metallurgical coke the size of the charge and compression give it great density and hardness. The coke from horizontal retorts, owing to the thin layer carbonised, is softer and looser in structure, and it was feared that in the continuous vertical retort, as the charge was always being moved on, that this failing would be accentuated. This, however, does

not seem to be the case, as is shown by the two photo-micrographs of sections of horizontal and continuous vertical retort cokes, taken from Mr Newbigging's Institution paper, in which



Coke from horizontals. Coke from verticals.

Fig. 25.—Photo-micrographs of coke.

he gave also the following details as to other physical properties of the two cokes, which are all in favour of the vertical product from the gas manager's point of view.

Comparison of Coke from Vertical and Horizontal Retorts

	Coke from Vertical Retorts.	Coke from Horizontal Retorts.
Apparent specific gravity	1·079	0·915
Real specific gravity	1·800	1·706
Pores in coke . .	40·06 % by vol.	46·37% by vol.
Volatile matter . .	0·69	3·73
Evaporative value .	13·85 lbs.	13·4 lbs.

If only in the manufacture of gas the coke could be improved so as to fit it for domestic use, the creation of a large market would enable a reduction in the price of gas to be made that would still further increase its use as a fuel.

I am sure in my own mind that these are the lines which the gas industry should consider seriously, and that the advances in the next ten years must be an endeavour to get nearer the ideal of carbonisation, and improve both gas and coke.

Various coals differ very widely in the amount of their expansion during the period of coking, although there may not be much difference in the composition of the coals. An interesting research on this point has been carried out by Dr R. Lessing, and the results obtained by him are certainly very striking. The apparatus employed by him consists of an outer tube of silica, closed at the bottom, round which is wrapped a coil of platinum wire, suitably insulated to prevent radiation losses; the platinum wire can be made hot by an electric current, and provides the necessary heat for the coking operation. In the outer tube fits loosely an inner tube, somewhat longer, and furnished with a side tube and stopper, and into this is weighed one gram of powdered coal of a definite fineness; on top of the coal is placed a solid piston made of quartz rod, which prevents the coal being blown out of the retort by the rush of gas when heating commences, but offers no obstruction to the swelling of the coal. The piston has a hook by means of which it can be lifted out of the tube after each test.

This method was found to be a great improvement on the ordinary laboratory method for determining the volatile matter in coal, as the influence of atmospheric oxygen in the heating is entirely eliminated, and also the resulting plug of coal gives a very good idea of the coking power of the coal treated.

The apparatus can also be applied to a determination of

the gas-making powers of a coal, and for this purpose the side tube of the inner silica tube is connected through a tar-collecting vessel to a measuring bottle. If required, the temperature in the little retort can be ascertained by a thermo-couple inserted through the stopper of the inner tube.

As with all the results obtained with the distillation of coal on a small scale, the figures obtained must be accepted with a certain amount of caution, as a laboratory test can never perfectly reproduce the results obtained in ordinary gasworks' practice. The method, however, should give useful indications, especially in the comparative testing of coals.

CHAPTER IX

THE NITROGEN AND SULPHUR OF COAL AND THEIR RECOVERY

Utilisation of nitrogen in agriculture—Yield of ammonium sulphate from coal and shale distillation—Nitrogen in vegetation—Percentage of nitrogen in coal and peat—Nitrogen in various coals—Yield of ammonium sulphate per ton of coal—The work of Forster, Watson Smith, and M'Leod on the distribution of nitrogen in coal distillation—Beilby's estimation of the nitrogen—Nitrogen in coke—Percentage of ammonia with increase of temperature—Tervet's experiments—The work of Ramsay and Young on the yield of ammonia—Yield of ammonia per ton of coal—The liming of coal—Formation of ammonia liquor—Composition of the liquor—Coke oven and blast furnace liquors—Ammonia compounds present in the liquor—Free and fixed ammonia—The manufacture of sulphate—Theories of the formation of ammonia during distillation—The influence of dilution—Cyanogen and cyanides—Sulphur in coal—Organic sulphur compounds in coal—Disulphide of iron and its relation to spontaneous ignition.

One of the most important factors in all manurial treatment of ground for agriculture is nitrogen (which can be fixed from the atmosphere by the plant during its growth only to a very limited extent), and upon which the growth of cereals in sufficient quantity to supply the demands of an increasing population is very largely dependent. It is only in certain forms that the nitrogen can be presented to the plant in such a way that it can be assimilated; and the salts of ammonium and nitrates have been the compounds universally used. The sources of the nitrates are limited, and their consumption has grown with even greater rapidity than that of coal. Whereas in 1880 only a quarter of a million tons were employed, during the last year a million and a half tons were used.

The chief source of this vast supply of nitrogenous material are those great nitrate beds in Chili at Tarapaca, and the more recently discovered deposits of Antofagasta and Tocopilla, which supply nine-tenths of the nitrate used for top dressing where backward growths have to be stimulated as rapidly as possible.

The great drain upon these deposits, however, threatens their exhaustion, probably within the present century, and as no further deposits of sufficient size to prove profitable have been found elsewhere, the necessity for such nitrogenous stimulants to plant life has led to innumerable attempts to produce ammonium salts, such as ammonium sulphate, which can be made from the ammonia recoverable from coal distilled at the gasworks and coke ovens, as well as from slack in processes of the Mond type, and is one of the most paying residuals.

The proportion of ammonium sulphate produced in this country from the destructive distillation of coal and shale was :—

Gasworks . . .	65 per cent.
Shale oil distilleries . .	19 ,,
Blast furnaces . .	9 ,,
Coke ovens . . .	7 ,,

but the yield from the latter source has largely increased. The total output is roughly 260,000 tons per annum ; but the demand for it in every country as a fertiliser is so great that the supply might be increased to an enormous extent without affecting the market ; and one of the greatest problems of the present century is how to best supply the nitrogen compounds essential for raising the wheat demanded to supply the ever-increasing population.

Nitrogen, which constitutes approximately four-fifths of our atmosphere, can be assimilated from air by the growing plant only to a very limited extent, and the inertia shown by

this element towards direct combination renders the problem of fixing atmospheric nitrogen in a form in which it can be utilised an extremely difficult one. Although in countries where abundant water power gives cheap electricity, nitrogen can be recovered synthetically, or by means of carbides, from the air and converted into ammonia, the traces of nitrogen locked up in our coal measures still constitute the cheapest source of supply of such nitrogen compounds, as ammonia (NH_3), which in combination with sulphuric acid yields sulphate of ammonium.

In growing vegetation small traces of nitrogen are found in so firm a condition of combination that it seems to defy the changes taking place in the conversion of the vegetable bases into our natural fuels. Some forms of plant contain more nitrogen than others, but as a rule 0·1 to 0·2 per cent. will represent fairly the amount present ; and the facts that little is disengaged during the process of change and degradation of the vegetable matter and that coal contains only a fraction of the weight of the original deposit from which it was formed would account for coal containing from 1 to 2 per cent. of it in combination.

Peat, however, which is looked upon by most authorities as an intermediate stage in the conversion of vegetable matter, often contains more nitrogen than coal. Whilst the highest amount I have ever found in coal is 1·8 per cent., I have found 2·5 and even 3 per cent. in specially rich peats ; so that it is probable that in its growth or decay the sphagnum has a special power of direct absorption and assimilation of nitrogen from the air.

So constant is the quantity of nitrogen in coal that the French observers of the last century considered that in making an ultimate analysis it was quite sufficiently accurate to estimate the ash, carbon, hydrogen and sulphur of the coal and take the oxygen by difference, allowing a constant 1 as the percentage of nitrogen. Since the introduction, however,

of less laborious methods of analysis the nitrogen is generally determined, and we know now that 1·4 would be a fairer average than the unit originally taken. The following table shows how small the variation in quantity is in coals from widely separated sources :—

NITROGEN IN COAL (SCHILLING)

Westphalian coal . .	1·50 to 1·49	Average	1·50
Saar coal . . .	1·09 1·02	,,	1·06
Silesian coal . . .	1·38 1·35	,,	1·35
Bohemian coal . .	1·38 1·34	,,	1·36
Saxony coal . . .	1·25 1·15	,,	1·20
English coal . . .	1·49 1·40	,,	1·45
Pilsener coal . . .	1·51 1·46	,,	1·49
Bohemian lignite . .	0·56 0·48	,,	0·52

If we take 1·4 per cent. of nitrogen as the average amount present in English coals, this is equal to 31·36 pounds of nitrogen, or 147·8 pounds of sulphate of ammonium per ton of coal. But the amount we can obtain is only a small fraction of this, for reasons we shall fully discuss.

Dr Beilby has given the average yield of sulphate of ammonium from the carbonisation of a ton of coal as follows :—

Coke ovens . .	19·7 lbs., or 13·3%	of possible.
Blast furnaces .	20·2 13·7	,,
Gasworks . .	22·4 15·1	,,

The modern methods of carbonisation in gas manufacture, however, by improving the conditions under which the gas leaves the heated mass of coal, have raised the yield of sulphate of ammonium to about 30 lbs. per ton. If, however, power gas and not illuminating gas is needed and no coke is required, the injection of excess of steam into coal undergoing a low temperature combustion largely increases the yield of ammonia, and from 65 to 90 lbs. of ammonium sulphate can

be made per ton of slack gasified. This has been a great factor in cheapening power gas, and also helping to supply the demand for sulphate, which is almost unlimited, and which must increase as the sodium nitrate deposits get more and more depleted. But in gas and coke manufacture the temperatures needed to get high yield of gas and hard coke destroy a considerable percentage of the ammonia, and reduce the average yield per ton to the figures quoted above.

When coal undergoes destructive distillation, the nitrogen it contains is distributed amongst the products. The proportions were originally determined by W. Forster, and published in the *Chemical Society's Transactions* in 1883. He employed for his experiments a Durham coal, known for its ammonia-producing capabilities, and having the composition :—

Carbon . . .	84·34
Hydrogen . . .	5·30
Oxygen . . .	4·29
Nitrogen . . .	1·73
Sulphur . . .	0·78
Moisture . . .	1·14
Ash	2·42

The nitrogen was found distributed on destructive distillation as follows :—

Evolved as ammonia . . .	0·251
,, as cyanogen . . .	0·027
Remaining in coke	0·842
	1·120

He surmises that the missing 0·610 is present as free nitrogen in the gas, although " some, no doubt, is in the tar."

If these figures are reduced to the percentages of the nitrogen present in the coal we obtain :—

	Per cent.
As ammonia . . .	14·50
As cyanogen . . .	1·56
In coal gas	35·26
In coke	48·68

Watson Smith, in criticising this paper, showed that the tar contained a considerable proportion of nitrogen, amounting to 1·667 in the tar, and on distillation the various fractions contained nitrogen in the following percentages :—

Crude benzene . . .	2·327
Light oil	2·186
Creosote oil	2·005
Red oil from anthracene .	2·194
Pitch	1·595

He also found that Lancashire coal tars contain on an average as much as 2 per cent. of nitrogen, and points out that the distribution of the nitrogen through all fractions of the tar was to be expected, as the lighter naphthas contain the pyridine bases, the intermediate oils the quinoline bases, whilst the anthracene oils and pitch will contain the carbazols and acridine and probably other nitrogenous bodies of high boiling and melting point.

He also examined three samples of coke and found :—

	Nitrogen. Per cent.
Ordinary gas coke . . .	1·375
Beehive oven coke . . .	0·511
Simon-Carvès coke . . .	0·384

Showing that the short sharp heat of the gas retort was not so efficacious in driving out the nitrogen as a long continued high heat of the kind found in the coke ovens.

Since that date many estimations of the distribution of the nitrogen in the coal amongst the products of its distillation

have been made, by Knublauch, Landin, and others, but one of the most satisfactorily carried out researches on this point, made under ordinary working conditions, was that of McLeod in 1907. The summary of his results gives :—

Nitrogen in the coke . .	58·3
,, ,, tar . . .	3·9
,, ,, liquor . .	17·1
,, ,, cyanogen .	1·2
,, ,, gas . .	19·5

As might be expected, the most variable factor in all determinations of the distribution of the nitrogen in the coal is the amount that goes as free nitrogen into the gas, as the difficulty of preventing admixture of atmospheric nitrogen through leakage into the retorts during distillation and into the gas during purification and sampling is very great ; but the point which stands out clearly in all determinations is the overwhelming preponderance of the amount of nitrogen left in the coke.

It has been pointed out also by several observers that the amount of nitrogen in the coal is by no means a reliable indication of the amount of that element that can be recovered from it. Some coals, poor in nitrogen, apparently hold it in a form available for recovery, and so giving good yields of ammonia and cyanogen, whilst other coals, rich in nitrogen, apparently contain it in a more resistant condition of combination, so that it is mostly left in the coke, and the yield of nitrogen compounds is low.

Dr George Beilby found that very much the same distribution of the nitrogen was to be found on distilling bituminous shales for the production of oil :—

As ammonia in watery distillates	17·0 % of the nitrogen.
In the oil as alkaloidal tars . .	20·4 ,,
In the residue or coke . .	62·6 ,,

On fractionating the oil the fractions all contained from 3·24 to 3·54 per cent. of nitrogen, whilst the coke contained 4·1 per cent. It seems probable that there is present a series of carbon hydrogen-nitrogen compounds of unbroken continuity, from the volatile picoline (C_6H_7N), pyridine, anilin, etc., up to pitchy or coke-like substances, which must form a large proportion of the coke residue, as carbazol ($C_{12}H_9N$), contains 8·38 per cent. of nitrogen, and phenylnaphthylcarbazol ($C_{16}H_{21}N$) contains 6·45 per cent., whilst the residue contains 4·1 per cent.

The wonderful stability of some of the nitrogenous constituents of the coal is shown by the fact that a coke residue that had been heated to nearly 1000° C. (1832° F.) in a current of hydrogen for over fourteen hours still contained 0·82 per cent. of nitrogen, after heating to whiteness 0·4 per cent., and after then being taken to bright whiteness in a smith's fire for several hours it still contained 0·25 per cent.

The temperatures at which ammonia begins to be evolved from coals differ considerably with various kinds. As Anderson and Roberts have pointed out, this suggests that the nitrogen-bearing bodies in them must also differ, whilst the fixed residue of coal—*i.e.* coke, derived from coals very different in character and coming from very different localities, contain practically the same quantity of nitrogen, when the cokes have been made at the same temperature and the other conditions have been kept constant. This undoubtedly points to the resistant residue consisting of some definite body like carbazol, which is not decomposed at the temperature of carbonisation. Six coals experimented with by Anderson and Roberts gave :—

	Nitrogen in Coal. Per cent.	Nitrogen in residue. Per cent.
Ell coal	1·53	1·83
Splint coal . . .	1·50	1·73
Kiltongue coal . . .	1·63	1·77
Bannockburn Main . .	1·89	1·80
Kilsyth coking coal . .	2·04	1·79
Lower Drumgray coal .	2·12	1·79

Although the character of the nitrogenous material left in the coke is fairly clear, the nature of the compounds in the coal which yield the ammonia during destructive distillation are purely a matter of surmise.

In an earlier investigation made by Anderson and Roberts they came to the conclusion that " a considerable part of the organic matter in coal consists of a complex compound comparatively rich in nitrogen and containing sulphur as well."

We have seen the wonderful tenacity with which the nitrogen clings to the coke. It is, therefore, a perfectly justifiable inference that that nitrogen is present in the coal in the body or bodies that do most towards forming the carbonaceous basis of the coke. We have also seen that the humus bodies in their degradation during the formation of coal are the ones that left the residuum of carbon, and also that, on carbonising, the humus bodies in the coal leave a large residue of carbon, whilst the resin bodies leave but little. This points to the humus as being the compound carrying the nitrogen. Again, we have seen from the work of Braconnot that in peat it is the humic acid that is the nitrogen-carrier. All of which points to these compounds in the coal being the ones that hold the nitrogen.

An experiment made by Anderson and Roberts indicates the same thing. They took a sample of dry ell coal and heated it in a current of dry carbon dioxide at a temperature of 300° to 315° C. (572° to 699° F.) for four hours, by which

time it had lost 9·5 per cent. in weight, and the composition of the substance before and after heating was :—

	Before.	After.
Carbon	80·74	82·67
Hydrogen . . .	5·07	5·32
Oxygen and Sulphur .	12·47	10·00
Nitrogen . . .	1·72	2·01

They then oxidised these residues by nitric acid, and dissolved them in ammonia, from which they could be precipitated by acids as flocculent precipitates. These were analysed and gave :—

	Before.	After.
Carbon	58·45	58·57
Hydrogen . . .	3·15	3·01
Oxygen	32·36	32·28
Nitrogen . . .	4·70	4·60
Sulphur	0·72	0·71
Ash	0·53	0·83

The bodies are clearly identical ; and the inference they draw is that the nitrogenous molecule in the ell coal remains intact even when the coal is subjected to a temperature of 300° to 315° C.

The point to which I want to draw attention in this experiment is that in heating the ell coal to 300° to 315° C. the change in its composition which took place was a decrease in the quantity of oxygen and an increase in the hydrogen, showing clearly that it was a humus body that was being decomposed. In a further experiment Anderson and Roberts found that evolution of ammonia started between 315° and 400° C. (572° and 752° F.).

The fact that ammonia was a low temperature product of the distillation of coal was made abundantly clear to me by the results obtained in the " Coalite " process, where the yield of sulphate of ammonium averaged 12 lbs. per ton of coal

carbonised at 420° C. (620° F.) and the fact is fully confirmed by Burgess and Wheeler in their researches upon the volatile constituents of coal, in which they decomposed different classes of coal at varying temperatures, and also subjected coal to a fractional distillation in a vacuum, and found in every case that the largest yield of ammonia took place with the lowest temperatures employed.

The results as regards ammonia, abstracted from their tables of results, are as follows :—

PERCENTAGE OF AMMONIA IN GAS EVOLVED.

Temperature of Distillation.	Bituminous Alloft's Silkstone Seam.	Semi-Bituminous Penrhycyber, S. Wales.	Anthracite Pontyberen, S. Wales.
15 to 350° C.	5·60	2·50	..
400	2·25	..	2·90
450	1·20	2·35	..
500	1·10	..	2·20
550	1·45	0·60	..
600	0·50	0·15	1·05
650	*nil.*	*nil.*	..

In their first paper they distilled the same coals at temperatures rising from 500° to 1100° C. (932° to 2012° F.), but not in a vacuum, and obtained :—

Temperature of Distillation	Bituminous Alloft's Silkstone Seam.	Semi-Bituminous Penrhycyber, S. Wales.	Anthracite Pontyberen, S. Wales.
500° C.	2·00	3·10	4·35
600	0·70	..	..
700	1·10	0·80	..
800	0·85	0·60	..
900	*nil.*	0·30	..
1000	*nil.*	0·20	..
1100	*nil.*	0·10	*nil.*

These experiments were made with two grams of coal. It will be noticed that the evolution of ammonia practically

ceases at the temperature when in practice the evolution of ammonia is reaching its maximum, this being due to the cause that renders all such experiments of little or no use in considering the actions taking place on a large scale, *i.e.* the absence of extended surface contact. Instead of each stage of the distillation being at a gradually increasing heat and in presence of the condensed liquids given by the primary actions, the whole of the coal is raised in two minutes to the retort temperature and the tar freely escapes, but little condensation taking place, enough, however, is converted into pitch to give good coking, which is typical of rapid carbonisation, the hot exterior of each particle decomposing some of the products passing out from the interior of the grain, no matter how finely it is ground.

The very fact, however, of the rapid removal of the products from the zone of action makes the experiments of great value from the scientific point of view, and the fact that a considerable proportion of ammonia is evolved below a temperature at which it is possible to be due to secondary reactions, indicates clearly the presence in the coal of a body or bodies capable of yielding it as a primary product of decomposition.

The ideas existing as to the source of the ammonia yielded by coal on carbonisation are based on experiments made in 1883 by Tervet, who showed that when a coal has been distilled at a red heat, and the rich hydrocarbon gases have just ceased coming off, a stream of hydrogen passed through the red-hot mass causes the formation of ammonia in considerable quantity. In his experiments he used charges of 100 grams of coals in a 4-inch iron tube. A series of tests in which the temperature of the tube and the flow of hydrogen were gradually increased gave the following results when calculated to pounds of sulphate of ammonia per ton of coal :—

	Lbs. per ton.
I. . .	29·65
II. . .	34·21
III. . .	34·21
IV. . .	45·61
V. . .	52·30
VI. . .	56·72
VII. . .	57·02

From the description of the experiments the temperatures probably ran from 800° to nearly 1000° C. (1472° to 1832° F.).

The explanation of the action taking place given by Tervet is that " the nitrogen existing in coke can be liberated in the form of ammonia, it being only necessary to bring the compound into a state of strain by subjecting it to the superior affinity which exists between the combined nitrogen in the coke and free hydrogen at a particular temperature and in a predominating atmosphere, which shall prevent it from subsequent decomposition."

Tervet also made experiments with other gases, and found that methane, carbon dioxide, and nitrogen had no action, and carbon monoxide very little, but the coke which had been submitted for hours to the action of these gases, which had ceased to wash out the smallest trace of ammonia, directly a stream of hydrogen was turned into the coke, ammonia in abundance appeared.

He concludes his paper by stating that low heats in carbonisation favour the retention of the nitrogen by the coke, and high temperatures favour the production of gas and ammonia. A fact, however, which must not be overlooked is that ammonia gas is very easily decomposed again by heat into nitrogen and hydrogen, and although a high temperature may favour the dislodgement of the nitrogen from the coke, and help the synthetic production of ammonia, yet the higher the temperature the greater will be the destruction of the ammonia molecules.

Ramsay and Young made a series of experiments to ascertain what the temperature was at which ammonia underwent decomposition by contact with a heated surface. They passed a slow stream of ammonia gas through a heated porcelain tube filled with broken pieces of porcelain, and obtained the following results :—

Temperature.	Percentage of Ammonia Decomposed.
500°C.	1·57
520	2·53
600	18·28
620	25·58
680	35·01
690	47·71
810–830	69·50

With an iron tube filled with broken porcelain, the action was more marked—

Temperature.	Percentage of Ammonia Decomposed.
507–527° C.	4·15
600	34·44
628	65·43
676–695	66·57
730	93·38
780	100·00

So that the decomposing point begins a little below 500° C. (732° F.), and the rate at which it proceeds at rising temperatures is influenced largely by the nature of the heated material, and also by the time of exposure and area of heated surface.

It is quite clear that if under the conditions existing in gas manufacture the decomposition of the ammonia proceeded at this rate and at these temperatures, no ammonia would ever be found in the gas, as it would be all decomposed at 800° to 900° C., whereas if the temperature which in practice gives the largest yield of ammonia be carefully noted, it is

when the coal is giving about 9500 cubic feet per ton, and we know that this corresponds to just about the temperature at which, from Ramsay and Young's experiments, all the ammonia ought to be destroyed.

The yield of ammonia per ton of an ordinary gas coal carbonised at various temperatures and the yields of gas for six-hour charges in an ordinary horizontal retort may be taken approximately as follows :—

Temperature.	Cubic Feet per Ton.	Lbs. of Ammonia recoverable per Ton.
400 to 500° C.	5,000	12
500 to 600	7,200	15
600 to 700	7,500	17
700 to 800	8,500	20
800 to 900	9,500	26
900 to 1000	10,500	24
1000 to 1100	11,000	20

We have seen from Anderson and Roberts' researches, which are fully confirmed by those of Burgess and Wheeler, that evolution of ammonia commences at from 315° to 400° C. (599° to 752° F.), with many coals, and—although as far as I know the fact has never been pointed out—it is impossible that the Tervet reaction can take place at this temperature, requiring as it does a red heat and abundance of hydrogen.

It is fairly certain that hydrogen is not a primary product of the decomposition of coal, and appears in the gas in large quantities only at temperatures certainly above 400° C. Moreover, it cannot be hydrogen formed by the action of carbon on moisture, because this commences according to Bunte, only above 600° C., so that one is forced to the conclusion that the ammonia which is formed below 500° C., and is in quantity sufficient to give 12 lbs. of sulphate of ammonia per ton of coal, is derived from a nitrogenous organic body or bodies decomposing at from 315° to 500° C. in such a way that it evolves its nitrogen direct as ammonia. It is

perfectly clear, however, that the Tervet reaction takes place at a higher temperature, and gives the further increase in the quantity of ammonia, which reaches its maximum at between 800° and 900° C., when hydrogen is being evolved in the largest quantity from the luting pitch in the coal, the very stronghold of the nitrogen molecule.

Burgess and Wheeler have shown that all the primary ammonia has come off at 650° C. (1208° F.), and they obtained no ammonia from the secondary synthesis, because the quantity of material taken was so small that the ammonia formed was decomposed at once owing to the small amount of diluting gas and enormous ratio of heating surface ; but there is no doubt that in ordinary carbonisation in retort chamber or oven the ammonia produced is due to two distinct sets of actions.

The question, however, has not been answered as to how it is that just at the temperatures found by Ramsay and Young to produce complete destruction of the ammonia, the largest yield is being given by the carbonising mass.

Their experiments show that if we take ammonia gas by itself, and pass it through an iron tube packed with broken porcelain, the gas is all decomposed at a temperature of 780° C., but if instead of using it pure the ammonia be diluted with coal gas so that only 15 per cent. is present, on passing through the tube only 80 per cent. is decomposed ; dilute it down to 10 per cent. and decomposition falls to about 30 per cent. ; reduce it to 5 per cent. and less than 20 per cent. of it is broken up ; so that in all probability, when the minute trace is formed by synthetic action in the retort even at 1100° C., only 10 to 15 per cent. is again broken down. This is undoubtedly the reason for its presence at a temperature so far above its point of decomposition.

A point which cannot be emphasised too strongly is that it is not every coal that will yield ammonia freely, and that analysis of the percentage of nitrogen present is no criterion

of this. This is true of both the low and high temperature reactions, and Anderson and Roberts found that there is a considerable difference in the temperature at which various coals begin to give off the low temperature ammonia, some evolving it at 350° C., whilst with others it does not appear until 480° C., and marked signs of differences of the same character are to be found in the Tervet reaction with various coals.

From the results of other experiments made by Anderson and Roberts showing that no part of the nitrogen of coal is liberated during carbonisation as free nitrogen, and the fact that it is always found in the gas, it is evidently due to the breaking up of ammonia in contact with heated surfaces.

Dr Beilby has pointed out that the structure of coal has a great deal to do with the way in which various kinds of coal hold the nitrogen, which influences its distribution amongst the products of destructive distillation. Splint, cannel, and coking coals show obvious differences in structure, and after coking these differences are accentuated. Splint and cannel not only retain the original form of the coal when coked, but also its organised structure, so that this porosity is akin to that of charcoal, whilst high ash adds to this property. Surface has an all-powerful influence in the decomposition of basic nitrogenous bodies to ammonia, and Grouven, in decomposing his peat tars for ammonia, had to pack his decomposing tubes with porous material; so that it is possible that the extra surface presented by the nature of some cokes may influence the decomposition.

The fact that combustion with soda-lime will convert the nitrogen of coal and coke into ammonia probably suggested to Cooper the idea of liming coal before carbonisation, to increase the yield of ammonia, and, according to his hopes, improve the quality of tar, gas, and coke. To do this $2\frac{1}{2}$ per cent. (of the weight of the coal) of lime was slaked and mixed with the coal. It was widely tried, but the results were so contradictory that the process gradually sank into oblivion.

It has been revived recently at Cheltenham in a slightly altered form; ground caustic lime to the extent of 1·79 to 2 per cent. was fed by a hopper on to the coal as it went through the coal breaker, a small jet of steam being introduced under the rollers of the breaker to cause the lime to cling to the broken-up pieces of coal. In this way, small as was the quantity of lime used, perfect admixture was attained, and after more than a year's experience of the process it was found that the sulphate of ammonia was increased by 1·88 lbs. per ton, *i.e.* from 24 to 25·28 lbs., the yield of gas increased and the sulphur in it reduced, whilst stopped ascension pipes, which had been a great trouble in the works, were done away with. If these results can be maintained, this revival certainly means a great advance, as the coke also seems to share in the general improvement.

During the ordinary practice of carbonising coals for gas manufacture 10 to 12 gallons of water, partly due to moisture in the coal, partly to hygroscopic moisture, and partly to water formed by the direct combination of some of the hydrogen and oxygen of the coal substance, are formed, and condensing largely in the hydraulic main carry down with them the ammonia and ammonia salts which have been formed by the combination of free ammonia gas with carbon dioxide, sulphur acids, and other bodies of an acid nature in the gas. The remainder of this is taken out in the condensers and scrubbers, and small traces may exist as far as the purifiers. The strong liquor from the hydraulic main and condensers and the wash water from the scrubbers, concentrated as far as possible by repeated use, are all led, with other condensation products, to the tar well, and there, separating by gravity, yield the ammonia liquor and tar.

The complexity of the compounds present in the liquor may be judged from the following table of analyses, taken from the Alkali Inspector's reports :—

AMMONIACAL LIQUOR FROM ENGLISH GASWORKS.

	1	2	3	4	5	6	7	8	9
Specific Gravity . . .	1·020	1·024	...	1·026	1·019	1·025	1·025	...	1·033
Cyanides	trace	...	...	trace	trace	...	...	trace	trace
Ferrocyanide	...	trace	...	...	..	trace	trace	...	...
Chloride (as HCl) . . .	0·006	0·620	...	0·685	0·12	trace	trace	trace	0·946
Ammonia, total	1·827	2·630	1·84	2·476	1·382	1·593	1·550	1·316	2·745
„ fixed	0·110	0·395	0·28	0·490	0·120	0·100	0·100	0·116	0·600
„ free	1·717	2·235	1·56	1·986	1·262	1·493	1·450	1·200	2·145
Hydrogen sulphide . . .	0·6256	0·634	0·397	0·629	0·100	0·068	0·064	0·093	0·709
Sulphur, total	0·633	0·6955	...	0·750	0·1366	...	...	...	0·8269
Carbon dioxide	0·860	2·023	1·39	2·019	1·493	1·819	1·830	1·485	2·365
Distribution of sulphur per cent.—									
As Sulphate	4·14	0·59	...	0·43	4·03	...	...	..	0·81
Sulphocyanide . . .	2·26	7·91	...	14·40	16·47	...	...	...	12·91
Thiosulphate . . .	0·55	5·66	...	6·24	10·83	...	...	...	8·94
Sulphide	93·05	85·83	...	78·93	68·67	...	...	...	77·33

During the process of coking coal in the oven the same set of actions takes place as in the retort, but they are spread over a considerably longer space of time, so that the coke nearest to the walls of the retort is baked for a very much longer period, and nitrogen, probably as ammonia, is evolved therefore to a large extent ; but the extra contact due to the bulk of the charge plays the same havoc with this that it does with the illuminating hydrocarbons, and as a result the yield of ammonium sulphate in lbs. per ton is below the average yield in gas manufacture. There is also a difference in the strength of the liquors condensed from the residuals, which is weaker in the case of the coke oven liquor than with that from gas, as the coal employed nearly always contains more moisture and pit water from the washing processes it has undergone, and every extra per cent. of moisture in the coal represents from 2 to 2½ gallons of water in the condensers.

The following table gives the analyses of three coke oven liquors, taken from the same reports as those of the gas liquor :—

	1	2	3
Specific gravity . . .	1·030	1·017	1·010
Cyanides	..	trace	..
Ferrocyanide . . .	..	..	..
Chloride (as HCl) . .	0·0716	0·392	trace
Ammonia, total . . .	1·542	1·613	0·364
,, fixed . .	0·242	0·239	0·114
,, free . .	1·300	1·374	0·250
Hydrogen sulphide . .	0·057	0·333	0·0017
Sulphur, total . . .	0·3754	0·3720	0·1651
Carbon dioxide . . .	2·315	1·170	0·481
Distribution of sulphur, per cent.—			
As Sulphate . . .	6·47	6·64	37·73
Sulphocyanide . .	7·04	8·42	16·84
Thiosulphate . .	72·19	0·71	44·46
Sulphide . . .	14·31	84·22	0·97

We have seen that another source of ammonia is to be found in those blast furnaces in which splint coal, located chiefly in the west of Scotland, is employed, and many of these are now fitted with recovery plants, the chief differences being a much greater volume of gas has to be dealt with, that there is more moisture present and therefore more liquor, and that slight variations are produced by air playing an important part in the actions taking place in the lower portion of the furnace, with the result that the sulphides and sulphocyanides, which have been abundant in the other forms of liquor, practically disappear.

The following table comes from the same source as the two previous tables :—

	1	2	3
Specific gravity . . .	1·005	1·010	1·009
Cyanides	..	..	trace
Ferrocyanide . . .	..	..	trace
Chloride (as HCl) . .	0·233	trace	trace
Ammonia, total . . .	0·162	0·385	0·329
,, fixed . . .	0·082	0·019	0·006
,, free . . .	0·080	0·368	0·323
Hydrogen sulphide . .	..	..	..
Sulphur, total . . .	0·0021	0·0066	0·0039
Carbon dioxide . . .	0·116	0·755	0·708
Distribution of sulphur, per cent.—			
As Sulphate . . .	42·86	30·30	38·46
Sulphocyanide . .	..	..	..
Thiosulphate . .	57·14	69·70	61·54
Sulphide . . .	..	..	..

In gas liquor, whether obtained from the gasworks, coke ovens, or blast furnaces, the ammonia is combined with any substances of an acid nature that may be present, and the following salts have been identified as being present in it :—

Volatile

Ammonium carbonates.
„ sulphide.
„ hydrosulphide.
„ cyanide.
„ acetate.

Fixed

Ammonium sulphide.
„ sulphite.
„ thiosulphate.
„ thiocarbonate.
„ chloride.
„ sulphocyanide.
„ ferrocyanide.

The first class of compounds is generally improperly called "free ammonia," because the mere action of boiling the liquor decomposes the salts and drives out ammonia, whilst the second class is spoken of as "fixed ammonia," because a strong caustic alkali has to be added before the ammonia is set free by the base of the alkali used forming a salt with the acid in combination with the ammonium, and liberating ammonia gas. Free ammonia in the true sense of the term is hardly, if ever, found in gas liquor, that is, uncombined, as the quantities of carbon dioxide and sulphur compounds are in excess of the ammonia as the gas leaves the retort, and, as cooling commences, combine with it.

Analyses of gas liquors are misleading, as it depends entirely upon the part of the condensing plant from which the liquor is taken as to what its composition is—that from the hydraulic main differing widely from the liquor obtained from the condensers, and this again from the product of the washers.

The liquors, however, are all mixed in the tar well. Its

value for making sulphate of ammonia is expressed in "ounces," which represents the number of ounces of pure sulphuric acid the ammonia in combination in the liquor is capable of combining with per gallon. A 10-ounce liquor is one a gallon of which requires 10 ounces of sulphuric acid of a specific gravity of 1·068 at 15° C. (59° F.) to form sulphate of ammonia with the salts in solution in the gallon of liquor.

Gas liquor is worked up into sulphate of ammonia by treating it with steam to drive out the "free ammonia," adding lime to break up the fixed salts, and again steaming. The ammonia liberated by the two steamings is then passed into sulphuric acid in a lead tank, and as the liquid becomes saturated, and the sulphate of ammonia crystals form, they are recovered by means of ladles, drained, washed and dried.

The process is generally a continuous one, and many different forms of plants have been devised for carrying it out.

We have seen from the work of Ramsay and Young that when ammonia gas alone is heated above 500° C. decomposition ensues, and also that dilution retards this process, so that in the stream of coal gas leaving the red-hot retort a considerable number of molecules have escaped destruction, whilst others have fallen a victim to contact with either red-hot coke or the carbonised surface of the retort. In the nascent condition, that is, at the moment they are born from a decomposing compound, and probably before the atoms have found their fellow atoms to form a molecule, the nascent elements commit indiscretions they would never dream of when settled down into a steady-going molecule, and under such conditions the nitrogen from decomposing ammonia will combine directly with red-hot carbon to form cyanogen and hydrocyanic acid. Other observers consider that it is a case of double decomposition between carbon monoxide and ammonia that yields the hydrocyanic acid.

Considerable light has been thrown on the course taken by the reactions by the researches of Bueb, Bergmann, and others. Dr Bueb tried the action of ammonia on charcoal at temperatures varying from 800° C. (1472° F.) to 1000° C. (1832° F.), and also at 1150° C. (2102° F.) to 1180° C. (2156° F.). It was found that at 800° C. about 4 per cent. of the nitrogen of the ammonia was converted into hydrocyanic acid, but that at a temperature of 1000° C. as much as 24 per cent. had been converted, and the remainder of the ammonia decomposed into free nitrogen and hydrogen. In order to try what would happen in the presence of coal gas, a mixture of ammonia and coal gas was employed and passed over the incandescent carbon, when 60 per cent. of the nitrogen of the ammonia was converted into hydrocyanic acid, 20 per cent. came off free, and 20 per cent. remained unchanged, this taking place at 1150° to 1180° C. The addition of coal gas to the ammonia may act in two ways in causing this great increase in the percentage of hydrocyanic acid formed :—

(1) The hydrocarbons in the coal gas may decompose, and by yielding nascent carbon increase the amount of reaction between the carbon and hydrogen ; or

(2) They may act merely as a diluent and so prevent too rapid decomposition of the ammonia, and give time for a better completion of the action.

In order to solve this point, two experiments were made at the same temperature as before, the one with coal gas and ammonia, the second with coal gas carburetted with pentane and ammonia, when it was found that the extra carbon yielded by the pentane did not increase the yield of hydrocyanic acid.

Kulmann had found that when carbon monoxide and ammonia are passed over spongy platinum some hydrocyanic acid is formed, and it was thought that perhaps carbon monoxide in the gas when passing over incandescent carbon acted in the same way on the ammonia. Experiments were

therefore made with mixtures of carbon monoxide and also generator gas mixed with ammonia by passing over incandescent carbon. The conclusion arrived at was that the greater yield of cyanogen obtained when ammonia is diluted with other gases is not due to any chemical interaction, but solely to the diluted ammonia being better able to resist resolution into hydrogen and nitrogen than when undiluted.

It would serve no useful purpose to reproduce the details of all the experiments, but those with mixed coal gas and ammonia are of value as showing the influence of dilution in saving ammonia from decomposition at temperatures far above the point at which it would be broken up entirely if undiluted, and also the increase in the production of hydrocyanic acid :—

	I	II	III	IV	V
Duration of experiment—minutes .	33	47	150	180	185
Temperature, °C.	1100	1100	1040	1100	1100
„ °F.	2012	2012	1904	2012	2012
Per cent. ammonia in mixture .	8·7	9·6	12·0	13	14
Grams per hour	6·6	1·8	8·6	0·3	0·2
Percentage of nitrogen—					
Found as hydrocyanic acid .	19·1	22·8	31·0	46·6	52·5
„ unchanged ammonia	69·2	35·4	51·0	21·0	19·0
„ gas (free nitrogen) .	11·7	41·8	18·0	32·4	28·5

The most favourable temperature for formation of cyanogen varies according to the nature of the diluent. With carbon monoxide, generator gas, and with mixtures of nitrogen and hydrogen, it lies between 1000° and 1100° C., but with coal gas rich in hydrocarbons the best temperature is slightly higher.

Langlois, Kuhlmann, and St Claire Deville all considered that ammonium cyanide was formed and was stable at high temperatures ; but this view apparently is erroneous, and the survival of the hydrocyanic acid as well as the ammonia at the heat of the retort is due entirely to dilution.

The formation of cyanides during destructive distillation has been ascribed also to the action of carbon disulphide on

ammonia at a high temperature; but it does not seem reasonable to suppose that the ammonia should interact with traces of carbon disulphide when in presence of such enormously larger quantities of red-hot carbon and hydrocarbons of greater ease of decomposition, and it has also been suggested that it may be formed by the double decomposition of ammonia and methane.

In spite of cyanides being formed by the action of ammonia during decomposition, it does not at all follow that a good yield of the one means a bad yield of the other. The amount of both that we recover are, after all, only remnants, and the yield depends largely on conditions, such as the amount of dilution and the degree of heat to which they are subjected. As Mr Mueller has pointed out, simultaneous high or low yields of both are quite as frequently found as a high yield of the one at the expense of the other.

When iron purification for the gas is used cyanogen combines with the hydrated iron oxide to form ferrocyanide, which reduces the purifying power for sulphuretted hydrogen, and in the gas it has also a corrosive action on iron, as where rusting has started the cyanogen again forms ferrocyanides and seems to accelerate the corrosion.

The reason why ammonium cyanide is not formed, or if it is, only in very small traces, is because both carbon dioxide and sulphuretted hydrogen can turn it out of combination. If it were not for this hydrocyanic acid could never get past the scrubbers; but if it does combine with ammonium the ammonium cyanide would be decomposed to ammonium carbonate and sulphide and the hydrocyanic acid be again liberated.

When, however, cyanogen or hydrocyanic acid combines with iron to form hydroferrocyanic acid the ferrocyanide is not decomposed by either carbon dioxide or sulphuretted hydrogen. The same is true of sulphocyanic acid (HCNS). This is the basis of the wet methods employed for the

extraction of cyanogen from the gas. In the one process the gas is washed with ammonia liquor in which sulphur has been dissolved, so as to form ammonium polysulphides, which absorb the hydrocyanic acid in the gas, forming ammonium sulphocyanide, whilst in the other process or processes (for there are several) the gas is scrubbed with an alkaline solution containing an oxide, hydrate, or salt of iron which, absorbing the cyanogen, forms the ferrocyanide.

Coal invariably contains sulphur, and, although in many kinds the amount is small, it is a great drawback to its use for many purposes. The amount present in typical English coals and its resistance to heat, as shown by the amount still retained by the coke during the ordinary carbonisation in a retort, is shown by the following analyses made by Constam and Kolbe.

	Sulphur in Coal. Per cent.	Sulphur in Coke. Per cent.
Nottingham, bright co[illegible] .	1·10	0·83
Lancashire, Trencherb[illegible] .	0·85	0·73
Nottingham, best hard . . .	0·61	0·43
Kinneil	1·23	1·65
Durham, Low main seam . .	0·64	0·71
Durham, Hutton seam . .	0·81	0·69
Yorkshire, Barnsley	0·61	0·43
Durham, Ballarat seam . . .	0·42	0·54
Welsh, Nixon's Navigation .	1·07	1·11

The sulphur is present in the coal in several forms, in some we find gypsum or sulphate of lime, disulphide of iron, known as pyrites or coal brasses, and also organic sulphur compounds, about the nature of which we know nothing.

Drown, Helm, and Muck all drew attention to this organic sulphur in the early 'eighties, and it had been thought to be present by Percy at a much earlier date. Helm, having noticed that vapours containing sulphur are evolved by coal when heated at a temperature well below the boiling point

of sulphur or the decomposing point of pyrites, came to the conclusion that they must be due to organic compounds of sulphur, and attempted to extract the body that yielded them by such solvents as alcohol, petrol, potash, etc., but not succeeding, he determined the iron, sulphuric acid, and total sulphur from two English coals, and obtained the following result :—

	Organic Sulphur.	Sulphur as Pyrites.
I.	0·372	0·232
II.	0·818	0·102

Muck in 1886 confirmed the presence of organic sulphur in coal, and came to the conclusion that the distribution of the sulphur of the coal amongst the products of its carbonisation depended largely upon the character of the mineral constituents of the ash. If, for instance, a coal contains much oxide, s[illegible] carbonate of iron, this is reduced to metallic iron [illegible] rbonisation, which combines with the sulphur a[illegible], and we find it present in the coke, whilst if there is [illegible] on to fix it, the sulphur is found in the gas and tar.

This is true probably to a certain extent, but we know that in burning a coal or a coke on a fire or in a furnace the ash is sometimes red with oxide of iron, which is taken as an indication that pyrites were present in the original coal to more than an average extent, and yet the sulphur is so resistant that it is found in the ash, as shown by the following analyses given by Percy :—

Coal of the Carboniferous Period.	Ash in coal, per cent.	Sulphur in coal, per cent.	Sulphur in ash, per cent.	Proportion sulphur of original ash.	Sulphur evolved in burning.
I. . .	7·360	0·789	9·464	0·696	0·093
II. . .	5·760	0·973	14·663	0·844	0·129
III. . .	16·530	3·264	18·174	2·424	0·840
IV. . .	48·316	1·746	2·798	1·352	0·394

The original source of the sulphur in coal is in all probability the calcium sulphate, of which 2 to 5 per cent. is found in the ashes of vegetation, and which still exists in coal ash. Under the influence of temperature, pressure, and heat in the presence of carbonaceous matter the sulphat slowly becomes reduced to sulphide, which in contact with iron salts, especially the carbonate dissolved in the carbonic acid in infiltering water, combines with the iron and forms sulphide and disulphide of iron.

This disulphide of iron, according to the conditions under which it is formed, is found in the coal sometimes as a dark powder closely resembling coal itself, sometimes in thin golden-looking layers in the cleavage of the coal, and sometimes in masses and veins of considerable size. It was this substance which was, and sometimes still is, credited with being the constituent of coal responsible for heating and spontaneous ignition, it being supposed that its rapid oxidation on contact with air when the coal was removed from the mine gave out sufficient heat during its conversion from sulphide to sulphate to ignite the coal, but the following table, due to Richters, shows clearly that some coals containing the least sulphur are the most inflammable :—

Degree of Self-inflammability.		Iron Pyrites. Per cent.	Water. Per cent.
Difficultly self-inflammable.	1	1·13	2·54
	2	1·01–3·04	2·75
	3	1·51	3·90
Medium.	4	1·20	4·50
	5	1·08	4·55
	6	1·15	4·75
Readily self-inflammable.	7	1·12	4·85
	8	1·00	9·01
	9	0·83	5·30
	10	1·35	4·85
	11	0·84	5·52

During the destructive distillation of coal one of the first compounds that shows itself with the water vapour and carbon dioxide is sulphuretted hydrogen, and also probably volatile organic sulphur compounds like thiophene (C_4H_4S), traces of which are obtained in ordinary coal tar, whilst it is more abundant in low temperature tar. Sulphuretted hydrogen is present in low temperature gas to the extent of 1·8 per cent., whilst at high temperatures the action of the sulphur on the red-hot carbon yields carbon disulphide. In the tar and liquor we find sulphuretted hydrogen, ammonium sulphide, ammonium sulphocyanide, sulphur dioxide, carbon disulphide, sulphur alcohols or mercaptans, and a series of thio-hydrocarbons, with boiling points from 84° C. to 225° C., with still a large proportion of the sulphur remaining in the coke.

CHAPTER X

MODERN COAL GAS

The primary products of the decomposition of coal by heat—Secondary decompositions at low temperature—Effect of heat upon the secondary products—Improvements in the gas obtained by new methods of carbonisation—The composition of the gas from Glover-West continuous vertical retorts—From Dessau vertical retorts—Advantages of continuous carbonisation—Composition of gas from ordinary horizontal retorts—The alteration of the standard of illuminating power—The calorific value of gases and the advantages of a calorific standard—The Settle-Padfield vertical retort—Suggestion for a continuous system of carbonisation—The autocarburetting process and its results—Its application to continuous carbonisation.

Having now reviewed the action of heat on the coal constituents, we are in a position to discuss the actions which have resulted in the gas manager being able to increase his yield per ton of coal from below 10,000 cubic feet to over 13,000.

We have seen that the primary products of the decomposition of coal by heat are :—

Water vapour.
Oxides of carbon.
Saturated hydrocarbons—methane, ethane, etc.
Unsaturated hydrocarbons.
Ammonia.
Sulphuretted hydrogen.
Liquid tar of a paraffinoid nature.

The first three constituents so overshadow the other gases

in proportion that the primary gases might almost be stated as :—

Water vapour.
Oxides of carbon.
Saturated hydrocarbons.

The lowest temperature, however, at which we can practically distil coal is 400° to 500° C. (752° to 932° F.), and secondary actions and decompositions having started, hydrogen makes its appearance, and the composition of the gas approximates to :—

Hydrogen		27·5
Saturated hydrocarbons—		
Methane	48	
Higher members	10·1	
	——	58·1
Unsaturated hydrocarbons		3·0
Carbon monoxide		7·3
Carbon dioxide		2·5
Nitrogen		1·6

The gas before iron purification contains about 1·8 per cent. of sulphuretted hydrogen.

The low temperature gas, of course, varies with the coal used, and the hydrogen is often below 18 per cent. ; and the saturated hydrocarbons up to 68 per cent.

One source of the increase in volume in high temperature gas is the breaking down of this primary gas by contact and radiant heat, and we will try to gain an idea of what this will amount to.

On passing this gas through a tube containing broken porcelain, to give plenty of contact, and heated to 1000° C. (1832° F.), we obtain a gain in volume of 11 per cent., and the composition is :—

Hydrogen	52·3
Methane	34·0
Unsaturated hydrocarbons	2·5
Carbon monoxide	8·8
Carbon dioxide	1·0
Nitrogen	1·4

so that the action has been an increase in hydrogen at the expense of the ethane and other hydrocarbons, and a deposit of carbon is found in the tube. This coal under ordinary low temperature conditions gave 4500 cubic feet per ton, so that the 11 per cent. increase meant 495 cubic feet. The coke yielded on heating to 1000° C. 5000 cubic feet of gas, and the original coal carbonised in six-hour charges yielded 11,200 cubic feet. The gas, therefore, was made up as follows :—

Primary gas	4500 = 40·2	per cent.
Degradation of gas	495 = 4·5	,,
Residue in coke	5000 = 44·7	,,
Gasified tar	1205 = 17·6	,,
	11,200	

Another example of the same kind may be taken, the figures being arrived at in a different way, and with the primary distillations at a slightly higher temperature.

With a good Durham coal capable of yielding 11,000 cubic feet of gas and 10 gallons of tar per ton when distilled under ordinary conditions at a temperature of about 1000° C., it is found that on carbonising at 600° C. it yields only 5000 cubic feet of gas, but 22 gallons of tar per ton, and the residue, on continuing the distillation at 1000° C. yields a further volume of 4500 cubic feet of gas, but no tar; so that removing the gas first formed and the tar vapour from the secondary reactions induced by high temperature has reduced the gas yield by some 1500 cubic feet per ton, and

increased the tar yield by 12 gallons. An examination of the tar shows that the 12 gallons gasified by direct distillation at high temperature consist of the lighter portions of the whole of the tar, which at this temperature is capable of producing 1200 cubic feet of gas, leaving 300 cubic feet to represent the volume gained by degradation of gaseous hydrocarbons and deposition of free carbon, of which the high temperature tar contains 25 to 35 per cent.

It may be taken in round numbers, that when 11,000 cubic feet of gas are obtained per ton of such a coal, 45 per cent. of the volume is from the low temperature distillation ; 42 per cent. from the residues left in the low temperature coke distilled at a high temperature ; 13 per cent. from the various secondary actions and tar.

This gives us an idea of the amount of destruction of valuable material which is taking place with the light charges when we push temperatures in order to obtain big yields ; but the gas manager feels he is perfectly justified in doing it, as he gets 1000 cubic feet per ton more than when he used moderate heats, and, thanks to the No. 2 London argand, can fully satisfy his parliamentary obligations as to candle-power.

When tested by the No. 2 argand the low temperature gas has a candle-power of 22 ; the gas from the pitch in the coke is nearly non-luminous, giving not more than $2\frac{1}{2}$ to 3 candles, but when mixed with the rich gas in the proportions of 45 of the latter to 41 of the former gives a 16 to 17 candle gas ; whilst the gas from the tar and the secondary action is 10 candle gas when tested alone, and when mixed with the others brings down the total candle-power to 14 to 15 candles.

My views are that in pressing temperatures too high with light charges we are showing the same criminal waste of the natural advantages our country possesses that is shown by the man who generates power in an old-fashioned beam engine.

The hydrocarbon gases that we obtain when distilling coal in a rational way at rational temperatures are compounds containing volatile carbon, and in consequence an amount of energy that cannot be found in any compounds other than those obtained by the destructive distillation of coal, oil, shale, and natural fuel of this description, all of which is limited in quantity and must, in the ordinary course of events, be worked out or at any rate worked up to an unusable price within a period which is small indeed, as compared with the geological ages over which its production has spread, and our duty to posterity makes the degradation of these bodies by excessive temperature during carbonisation an indefensible crime. When we break up these hydrocarbons by heat we obtain gases that we could make at a third of their cost by other processes; and the importance of conserving the hydrocarbons and substituting diluents more cheaply made is a fundamental axiom which should be kept clearly in view.

A good example of the economy of not degrading primary hydrocarbons is to be found in modern carbonisation, in which a great advance has been unwittingly made in trying to obtain economies by the destructive distillation of larger charges of coal. In the new methods of carbonisation, where the makes approximate to 13,000 cubic feet, the improvement found is due entirely to the free escape without overheating of the products from the first two-thirds of the coal carbonised, whilst the extra volume is obtained from the complete degradation of the products from the remaining third. That this is so is shown by the methane in the gas. In all fair coal gas in which there has been no over-degradation, even if you have been getting 11,500 cubic feet per ton from light charges, the methane will be about 34 to 35 per cent. of the gas; but notice the products of the new carbonisation, and you will find plenty of samples with only 28 per cent., and some even lower.

For instance, in a paper read by Mr J. G. Newbigging in 1911, he gives a table of hourly tests, which show the beautiful uniformity of the gas as it leaves the Glover-West continuous retorts, but which also illustrates the point to which I want to draw attention :—

Time	a.m. 10·30	a.m. 11·30	p.m. 12·30	p.m. 1·30	p.m. 2·30	p.m. 3·30
Illuminating power : candles : No. 2 "Metropolitan" .	15·2	15·35	15·3	15·18	15·52	15·65
Calorific value gross .	548·6	546·6	540·7	554·2	556·2	552·2
Carbonic acid . .	0·8	0·9	0·8	0·8	0·8	0·8
Oxygen . . .	0·3	0·3	0·3	0·2	0·3	0·3
Unsat. hydrocarbons	2·8	2·8	2·8	2·74	3·1	3·1
Carbon monoxide .	6·3	6·5	6·5	6·10	6·5	6·5
Methane . . .	29·33	28·83	28·67	29·37	29·17	29·17
Hydrogen . . .	56·63	56·82	56·51	57·13	55·60	56·79
Nitrogen . . .	3·84	3·85	4·42	3·65	4·53	3·34
Grains H_2S at outlet from rotary washer per 1000 cu. ft. .	600	610	600	600	590	590

whilst in some other analyses of high yields with Lancashire and Derbyshire coal, the methane is 26·94 per cent. and 27·54 per cent. respectively.

Again, in a paper at the same meeting, Mr C. Drury gives the composition of the gas from his installation of Dessau verticals using Durham coal as :—

	Without Steam.	With Steam.
Carbon dioxide . . .	2·4	2·2
Illuminants . . .	3·9	3·4
Oxygen	0·3	0·4
Carbon monoxide . .	8·0	7·8
Methane	31·2	29·8
Hydrogen	49·3	51·6
Nitrogen	4·9	4·8

In considering the ultimate effect of pushing temperatures to the highest possible extent, it is well to consider the amount and value of the gas and coke that could possibly be obtained from an ordinary coal. If we took a coal of the composition—

Carbon	80
Hydrogen	5
Oxygen	10
Nitrogen and ash	5

and were to carbonise it in an inverted vertical retort with the coal fed in by a ram at the bottom, so that the gas and vapours had to traverse a column of ten feet of coke at 1000° C., contact would decompose all the gaseous and volatile compounds to hydrogen and carbon monoxide, and we should obtain approximately :—

Coke, 15·27 cwt.

Hydrogen . .	21,000 cubic feet per ton
Carbon monoxide .	5,300 ,, ,,
	26,300

That is, you would double the volume of gas ; but it is a non-luminous gas of the same thermal value (gross) as water gas, and not worth more than the 3½d. to 4d. a thousand that you could make water gas at by one of the newer processes. Certainly you get an increase in the quantity of coke, and it would be an excellent metallurgical coke.

This is exactly what is done in all the new processes directly the cool passage for the escape of the primary gases gets tar-logged, and the gas from the remaining coal is driven through the red-hot coke and along the sides of the retort. Under these conditions some 3500 cubic feet of 22 candle gas are obtained, whilst there is a free cool passage for its escape, and after that is closed the remaining coal

yields by complete degradation of the tar and hydrocarbons, hydrogen, and carbon monoxide to make up the total volume.

Of course there is the saving factor that between the good primary gas and the relics of ruined hydrocarbons there is a good deal of only partly destroyed gas from the coal and tar near to the mouthpiece, so that the make averages out at 15 candles, and the cool distillation of the tar from the first two-thirds of the coal yields two-thirds of the 20 gallons that would have been obtained had it all been distilled in the same way. This is the secret of the "new process tar" being 13 to 14 gallons per ton, more liquid, and more paraffinoid in its nature.

In continuous carbonisation it is claimed that degradation does not take place; but the make and the methane in the gas tell their own tale, and the fact that the charge is always fairly cool in the top three feet of the retort, and is of nearly the full breadth of the retort is made up for by the rapid tailing of the uncarbonised portion, which soon makes the cool inner core an impossibility, whilst it must be tar-logged for a considerable distance.

In all probability, as soon as the carbonisation has spread a couple of inches into the charge, the gas that is being evolved from the residues on the hot side of the tar wall will pass up through the hot zone and undergo complete decomposition, so that the signs of degradation in the gas are not to be wondered at; but there is no doubt that the new processes have done what has never been done before, that is, they save a large proportion of the primary products.

I have emphasised several times the fact that it is contact with highly heated surfaces and not radiant heat that is most active in destroying hydrocarbons. A proof of this to my mind is to be found in the composition of the gases evolved during successive stages in a light charge. The coal is charged into the red-hot retort and the crown is but little cooled, and soon recovers its temperature from the hot

upper flue, so that radiation is acting from the first. We have seen, however, that the top of the charge heats up only slowly and does not become red-hot for some time, as it has only radiant heat acting through eight or nine inches of gas to raise its temperature until the heat reaches it from below. This means that for the first hour of the carbonisation the gas is exposed to as much radiant heat as at any period of the distillation, but it is only well on into the period of carbonisation that contact with red-hot coke begins to act, so that in the earlier periods it is only the layer passing along in contact with the red-hot crown that suffers from its action.

No matter what temperature is used—the heats may be pressed as high as the material of the retorts and flues will stand—the temperature of the distillation of the coal will be the lowest temperature at which it evolves gas ; and if one looks back to Lewis Thompson Wright's classical work on the influence of temperature on carbonisation, it will be found that the coal fed into a retort at the highest temperature attainable gives for the first ten minutes a rush of gas having much the same composition as low temperature gas—

	Time after commencement of Carbonisation—			
	10 min.	1 hr. 30 min.	3 hrs. 25 min.	5 hrs. 35 min.
Hydrogen . .	20·10	38·08	50·68	67·12
Methane . .	57·38	44·03	35·54	22·58
Hydrocarbons .	10·62	5·98	3·04	1·79
Carbon monoxide	6·19	5·98	6·21	6·12
Carbon dioxide .	2·21	2·09	1·49	1·50
Sulphuretted hydrogen	1·30	1·42	0·49	0·11
Nitrogen . .	2·20	2·47	2·55	0·78
	100·00	100·00	100·00	100·00
Carbon density of hydrocarbons .	2·86	3·11	3·38	2·29

It will be seen that not only is the gas driven off in the first ten minutes of the charge nearly identical in composi-

tion with low temperature gas, but also that the gas yielded in the last period of carbonisation is nearly the same as the gas obtained by the further distillation of the low temperature coke, whilst during the intermediate five hours of the charge the gases evolved have been mixtures of the primary gas in various conditions of secondary change diluted with the residual gas from the partially coked coal on the exterior of the charge, the secondary changes being brought about by contact between the primary gas, the tar vapours, and the wall surface, passage through the skin of red-hot coke, and radiant heat.

We have seen that the whole history of gas manufacture has been a record of the endeavours made to obtain an ever-increasing volume of gas from a unit of coal, and that the only limiting factors to the gas manager's ardour have been the nature of the refractory material he has used in making the retorts and settings, and the standards of illuminating power which Parliament has from time to time imposed in the interests of the consumers.

During the first half century of the use of coal gas it was the life of the iron retort that held temperatures in check, and when at last after twenty years' rebellion against the idea of using fireclay in place of iron the gas manager took the plunge and adopted it, and had the means of pushing temperatures to a far higher degree than before a standard of candle-power was imposed, which, when as in the south of England sea-borne coals had to be used, not only prevented him from pressing temperatures to their utmost, but necessitated the use of cannel to ensure the gas fulfilling the parliamentary obligations after distribution over a large area.

Then came the shortening of the cannel supply and consequent rise in price, which led to oil being adopted in the form of carburetted water gas for enrichment purposes. This bridged over the ten years from 1889 to the end of the century, by which time the incandescent mantle, born in

1885 and struggling for existence until 1894, had obtained such a universal hold that every one had learnt the lesson that heat in the flame and not artificial enrichment in the gas was the real object at which to aim.

This induced Sir George Livesey to approach Parliament in 1900, and by paying heavily for it he got a reduction in candle-power. Other companies then applied for the same boon—at first singly, and latterly in batches. The result is that a universal lowering of candle-power has taken place.

As soon as the candle-power was lowered below 16 candles, it became evident that the London argand specially designed to burn a 16 candle gas made from coal and cannel only, was absolutely unfitted for the consumption of the leaner gas at the rate of 5 cubic feet per hour. A new standard burner was introduced in preference to tampering with the sacred 5 cubic feet per hour consumption, and this burner, known as the No. 2 argand, developes so much more perfectly the candle-power of the gas that the gas companies have had some trouble in getting down to the new standard.

The idea of a candle power standard was introduced as a protection for the flat-flame user, and having fulfilled its functions it should be buried with the flat-flame; and as at the present time the calorific value of the gas is the important factor in generating light, heat, and power by its use, surely the time has arrived when a calorific standard should take the place altogether of an illuminating one.

It has been noticed frequently that the gas from Continental gas ovens and chamber processes is in heating value quite up to English requirements, although the illuminating value has been only 10 to 12 candles. This is in many cases due to the fact that in such gas the benzene is low, and that the greater portion of the illuminating power is due to saturated hydrocarbons. The illuminating value of benzene vapour is so high that although its heating value is double

that of ethane, the percentage which will yield one candle to the lighting power of the gas will represent only 23 B.Th.U., whilst one candle power derived from ethane will bring up the heating value of the gas by 267 B.Th.U., or more than ten times as much.

	B.Th.U. gross per cub. ft.	Candle Power per 5 cub. ft.	B.Th.U. gross per candle.
Hydrogen . . .	325	*nil.*	*nil.*
Methane . . .	1024	5·2	985
Ethane . . .	1870	35·0	267
Propane . . .	2682	53·3	253
Ethylene . . .	1603	70·0	115
Benzene . . .	3718	820·0	23
Carbon monoxide .	342	*nil.*	*nil.*

In ordinary high temperature gas made in horizontals the chief illuminating value is due to ethylene and benzene, whilst ethane is low in volume or absent, whereas in the first half of the period of distilling gas from a modern vertical retort chamber or oven, the comparatively low temperature at which it escapes causes it to be rich in paraffin hydrocarbons, which add to the calorific value to a greater extent than to the illuminating value.

All the time that the exigencies of the illuminating power tests call for the production of benzene and ethylene, small charges, high temperatures, and cutting down the period of carbonisation to the point at which all volatile matter is expelled, will give the best results in volume and candle-power but directly the gas manager has to work to a calorific instead of an illuminating standard, the importance of getting the gas away without overheating will be recognised, and with the problem of how to gasify the largest proportion of the carbon in the coal before him, the paraffin hydrocarbons will take their proper position as the most important constituents of coal gas.

The ideals to be attempted in a perfect carbonising process are a uniform treatment of every particle of coal distilled, a uniform treatment of the whole of the gas evolved, and what is perhaps as important as anything, preventing the degradation of valuable hydrocarbons by contact with hot coke or other surfaces.

I have shown the limitations of the various processes, and there can be no doubt in the minds of those who have studied the question, that the continuous vertical retort, when properly proportioned and worked, gives the only solution of the problem of uniformity in treatment to coal and products alike; and if scientific teaching is of any value, they must be the type of gas-making retort in the future.

The modern forerunner of the vertical continuous process was, as I have already pointed out, the Settle-Padfield retort, which I tested at Exeter seven or eight years ago, and with the principle of which I was immensely taken, and which gave splendid results. Its passage, however, from the experimental to the practical scale, as in so many cases, proved its undoing. On looking up a notebook of that date, I find that I obtained the following results :—

Coal used—poor slack, No. 4 Cammerton.

Makes per ton.	Gas . . .	13,250 cubic feet.
	Illuminating power	14·75 candles (London argand).
	Heating value .	533·7 B.Th.U.
	Tar . . .	none.
Same coal in horizontal retort.	Gas . . .	9862 cubic feet.
	Illuminating power	15 candles.

The Settle-Padfield process consisted of a semi-vertical or, if I may call it so, boot-shaped retort, much of the same design as now used in shale distillation (Fig. 26, p. 288). The vertical portion was about six feet in length, and the inclined part at the bottom three feet, the junction of the two por-

tions being the weakest part of the apparatus, as it was liable to crack, thus leading to infiltration of furnace gases,

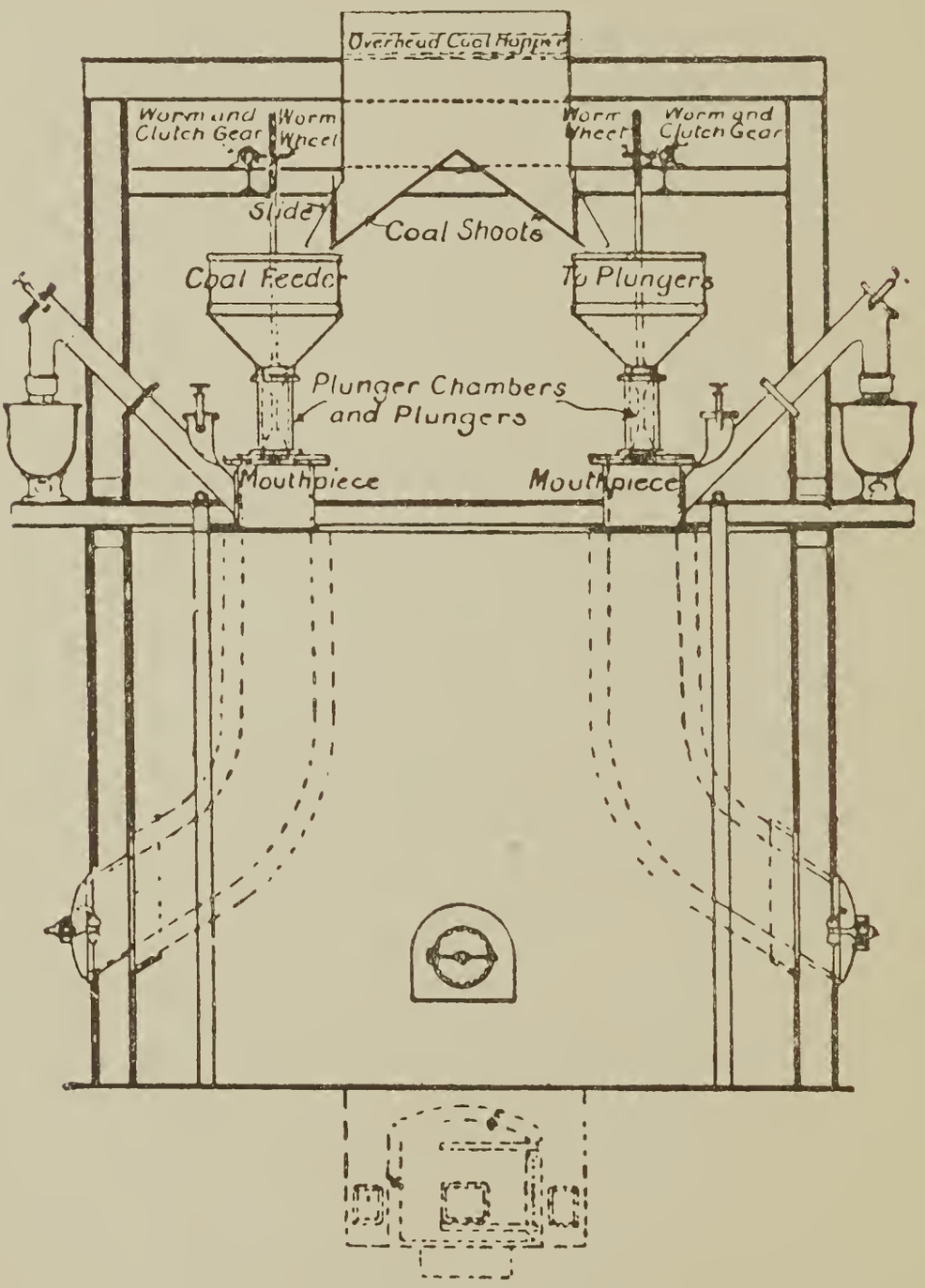


FIG. 26.—Settle-Padfield vertical retort.

which was discovered when the gas given in the above test was analysed. The leak was then made good, and further tests gave 13,000 to 13,200 cubic feet per ton of 15 candle gas.

The outstanding feature of the process was that the upper three or four feet of the vertical portion of the retort were left empty, and that the coal was fed in at the top by a

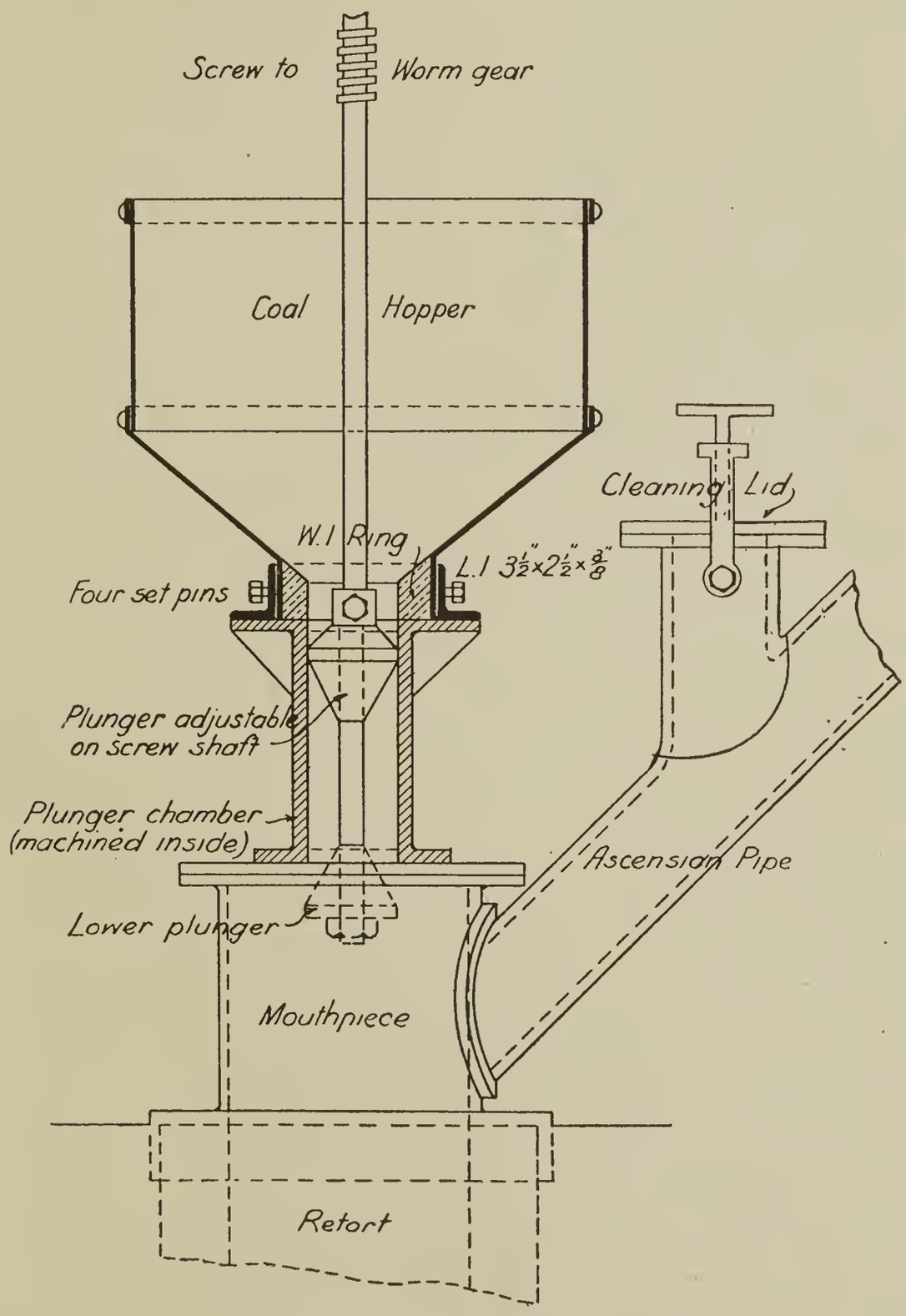


FIG. 27.—Top of Settle-Padfield Retort.

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plunger in charges of 2 to 7 lbs. per stroke as desired (Fig. 27), and fell through the empty heated zone on to the red-hot coke, where it was carbonised on the heated surface, the first run of rich gas rising straight up through a zone of radiant heat to the mouthpiece at the top of the retort.

The weakness in this process was that the coke was allowed to accumulate, and was then at intervals removed through an ordinary oven door at the bottom of the incline, so that the " baking area " varied according to the amount of coke at the bottom of the retort. Had the retort been a plain vertical one, with an automatic coke remover working *pro rata* with the coal feed, it would have been the perfect embodiment of the true conditions for carbonisation, as the temperature needed only a little lowering in the superheating portion of the retort. The idea was to carbonise all the tar formed. If any condensed, it was returned to the retort. This phase of the subject has already been discussed.

In the Settle-Padfield experimental retort I should say, speaking from memory, that the temperature in no part of the retort was 1000° C. (1832° F.), if so much, and yet at this temperature 13,000 cubic feet of gas per ton was made from Cammerton slack, the gas tested in the London argand giving 15 candles, which would have been 17·5 on the No. 2 argand. The same coal in a horizontal retort gave 9862 cubic feet of the same candle-power gas, and 10 gallons of tar per ton ; so that the alteration in the method of carbonising and the tar, which, if any formed, was returned to the retort, gave a gain of some 3000 cubic feet. The temperature of the lower portion, however, was insufficient to drive out all the more resistant volatile matter, and a very good coke was the result.

Now, what was it that caused that roughly erected old retort to give results better if anything than the beautiful models of constructive skill that we see in the two present continuous systems ?

In the first place, we all know the importance of a large ratio of heating surface to the mass of coal, and if you consider how the ground-up slack must have piled itself up on the top of the mass of red-hot material heated from below, washed by the ascending hot gases from the last charge, and radiated upon by the sides of the red-hot retort above, it is clear that the heating surface was far greater than in any other system, and instead of the heat penetrating slowly to the coal, it was plunged, the moment it left the feed, into a red-hot area, which drove off a good deal of the gas before even it reached the carbonising mass below, and deposited it sweating tar on the hot surface. The gases as they were disengaged rushed straight upwards to the exit without coming in contact with any surface to decompose them, the radiant heat being just sufficient to fix and get the best out of the tar vapour.

To many the idea of a heated space above the carbonising coal seems like going back to the lightly charged horizontal with the space that led to disaster; but they do not realise that radiant heat does little harm and much good, if there is not too much of it, and that it is contact with hot surfaces that is fatal. In the horizontal the gases rushed up to the top of the arch and were decomposed by contact with it, depositing their carbon as scurf on its surface, whilst in a vertical space they rush to the cool top and exit pipe, hardly touching the sides, whilst the radiant heat performs such beneficent functions as breaking up the hexahydrides in the tar vapour into aromatic hydrocarbons and free hydrogen.

Mr W. G. Africa, in a paper read in October 1911 at St. Louis, in relating his experience with vertical retorts, says that they got unusually high results as to candle-power by leaving a space of four feet of heated retort above the coal, thus fixing the vapours, which in full retorts do not reach the proper temperature for gasification.

My idea of a perfect continuous system would be a vertical

retort, like the one that Glover first made, which had the space at the top, and to have it fitted with a semi-intermittent feed and coke remover device, with the addition of the cooling chamber, with secondary air regeneration, the heat in the flues being concentrated on the outside of the retort at the spot where the coal falls on to the surface of the coke, as it is here that heat is withdrawn most rapidly. The temperature might then fade away above and below this area to, say, 800° C. (1472° F.). If properly regulated, 6 to 8 per cent. of the volatile matter of the poor gas-forming residues would be left in the coke to make a perfect domestic fuel, any shortage of gas being made up with blue water gas.

The volume of gas actually made from the coal might be only 9500 to 10,000 cubic feet, but it would be rich in saturated hydrocarbons, and would stand dilution with probably 5000 cubic feet of water gas used, as I shall suggest, to bring it down to statutory requirements. In this way it should be possible to make more gas than at present and a valuable fuel, whilst we should have attained practically the ideal of carbonisation—uniformity.

It will be remembered that I have already pointed out the importance of the coal undergoing carbonisation being reduced to a uniform size, and that the size should be the smallest practicable to use. There is no need for a powder so fine that the uprush of gas would cause loss, but pieces so large that the outside has a chance of becoming red hot before all the gas has escaped from the interior should be avoided. Moreover, the coke is to be a domestic fuel, and the using small coal for its production will, in the case of coals that need it, allow of washing. At 4d. to 6d. a ton this is well worth doing, as the sulphurous fumes from ordinary gas coke is one of the features to which the public takes strongest exception.

The basis of the method of carbonising coal which I

propose, and which will give the nearest approach to ideal conditions that it is possible to attain, is to plunge fine coal into an atmosphere of gas at such a temperature as to drive out most of its gas before it reaches the state of rest, and to complete the elimination of the rich gas in a current of red-hot poor gas passing up from the coke residues in the mass below. This is to take place under the influence of radiant heat ; and to ensure the minimum of decomposition I should propose to use the water gas, which would have to be employed in any case to bring the gas down to the required standard of light and heat, to increase dilution in the superheating zone.

I venture to think that water gas has never been used by the gas manager under proper conditions, save in making carburetted water gas, where it goes red hot from the generator into the cracking chamber, where the hot brickwork is decomposing the oil. When blue water gas has been employed *per se* as a diluent it has been used either cold or so little heated as to be far below the temperature of the gas which was to carburet it.

Under these conditions it is not easy to get a perfect mixture in large volumes of flowing gases, as in spite of the laws of diffusion, layering is very apt to take place. On the Continent, where the price of oil is a set-back to carburetted water gas, blue gas is often used, and to ensure proper mixing it is passed into the foul main or, in some cases, through the retorts themselves, as proposed by me ; but in no case is the water gas properly heated, and a chill of only a few degrees to carbonising coal is fatal to good results.

The old " auto-carburetting " process, which I suggested in 1900, is well worthy of consideration at this juncture. In laboratory experiments using superheated water gas, magnificent results were obtained, but in the experiments made on a large scale at the Crystal Palace gasworks it was not possible to properly heat it. In these experiments a Derby-

shire coal was employed, and the yield of gas and candle-power given by the gas were tested on a large scale before, during, and after the water gas experiments. It was found that under ordinary conditions of carbonisation the coal yielded 10,468 cubic feet per ton, of 15·88 candle-power gas.

The plant used in the earlier experiment consisted of six beds of seven retorts each, and later of twelve beds of seven retorts. The section of all retorts was 22 inches by 16 inches and 20 feet long. They were heated by regenerative furnaces and charged by power-stoking machinery. The gas from them was passed through one complete section of the works separately, and was therefore condensed, scrubbed, purified, and measured in the usual way—the ordinary gas manufacture being carried on at the time in other sections of the works.

The water gas was made in the ordinary "Economical" water gas plant, and conveyed from the relief holder to the retort house by a special pipe. This pipe was continued over the retort bench, just above the arch pipes on one side, and a connection was made from it to the top of each ascension pipe on that side of the bench. Each connection was fitted with a cock having a lever handle with rod attached to it, so that the cock could be regulated from the charging floor. The dip pipes on this side were blocked, and the hydraulic main valves closed. The water gas therefore descended the ascension pipes on this side, passed through the retort, and up the ascension pipes on the other side along with the coal gas.

The quantity of water gas which could be passed through each cock, when partly and when fully open, was ascertained before the test by measurement through a meter. This enabled an approximate measurement of the quantity of water gas put into each retort to be made ; but the actual quantity used in each experiment was checked by noting the quantity taken out of the holder. The heat of the

retort was maintained as nearly uniform as possible throughout the tests, and at as high a temperature as is used in ordinary working.

Many experiments were made in this way, all of which showed that important economies could be attained by the process. The following experiment will give an idea of the result obtained by using 40 per cent. of blue water gas in this way as compared with 40 per cent. simply mixed with the coal gas :—

Coal carbonised	82 tons.
Make of mixed gas per ton . .	13,730 cubic feet.
Water gas added per ton . .	4005 ,,
Proportion water gas added .	4·1 per cent.
Proportion water gas in mixture .	29·1 ,,
Candle-power	14·87 candles.

Candle feet—

$$\frac{13{,}730 \times 14{\cdot}87}{5} = 40{,}833 \text{ candles.}$$

Standard—

$$\frac{10{,}468 \times 15{\cdot}88}{5} = 33{,}246 \text{ candles.}$$

Gain in candle feet on standard . 25 per cent.

Analysis of gas	I	II
Hydrogen . . .	50·37	50·62
Saturated hydrocarbons .	29·24	29·49
Unsaturated hydrocarbons	2·98	2·48
Carbon dioxide . .	0·49	0·49
Carbon monoxide . .	14·92	14·92
Oxygen . . .	*nil.*	*nil.*
Nitrogen . . .	2·00	2·00
	100·00	100·00

Calorific Value—

Calories gross	. . 149·8	net 132·9
B.Th.U. „	. . 599·2	„ 531·6

These experiments were renewed in 1901 with inclined retorts instead of horizontal, and a bench of seventy inclined retorts, which had been newly erected, was utilised for the purpose. The water gas was made, as in the previous experiments, in the generator of the "Economical" plant usually employed for the manufacture of carburetted water gas. The gas was passed into a holder of 469,800 cubic feet capacity and thence was carried to the inclined retorts, into which it entered at atmospheric temperature. The gas was not purified before being admitted to the retorts, but was tested for carbon dioxide, of which it contained from 5 to 6 per cent. The carbon dioxide, after estimation, was deducted by calculation from the volume of water gas used, because the volume of mixed gas produced was measured in station meters after the whole of the carbon dioxide had been removed by purification in the usual manner.

To ascertain whether the carbon dioxide in the water gas was converted into carbon monoxide by passage through the retorts, the mixed gas was examined at the inlet to the washers, and found to contain 3 per cent. of carbon dioxide. It may be assumed, therefore, that the carbon dioxide as it passed through the retorts was not converted to any appreciable extent into carbon monoxide.

No station meter could be placed at my disposal for the measurement of the water gas. The holder of known capacity (469,800 cubic feet) was therefore filled before the commencement of each experiment, no gas being admitted to the holder during any trial. The volume of the gas was obtained by recording the height of the holder at the commencement and completion of the experiment, and making

all the necessary corrections for temperature and pressure. The quantity of water gas used during 24 hours varied in the different experiments from 200,000 to 370,000 cubic feet. The gas leaving the retorts was purified in the usual manner, and then passed through station meters, from which readings were made every hour.

During every hour the gas was slowly by-passed into a small holder, from which gas was drawn at the completion of each hour for the determination of the illuminating power by means of the Referees' table photometer, and from this once every day gas was drawn for analysis and for the determination of its calorific value by means of a Junkers' calorimeter.

The coal used in the experiments was the same kind of Derbyshire coal as had been used in the previous tests, but of slightly inferior quality. Before commencing the experiments with water gas, a trial run was made for seven days with the coal alone, the tests being made every hour, day and night, so as to obtain a standard for comparison. The principal results obtained were :—

Total coal carbonised .	603 tons.
Total gas made (corrected)	5,973,682 cub. ft.
Make per ton . . .	9,907 cub. ft.
Average illuminating power (table photometer) .	16·55 candles.
Total tar (hydraulic) .	5060 gallons.
Tar per ton . . .	8·3 gallons.
Calorific power, gross .	152·6 calories per cu. ft.
,, net . .	138·8 ,, ,,

These figures give the value of 32,792 candle feet per ton for the coal. This figure is taken as the standard in the following experiments.

In arranging the apparatus for the experiments, the upper

mouthpiece of each retort was fitted with a pipe and stop-cock for the admission of the water gas.

These experiments were continued from June 19th to August 23rd, 1901. Passage of water gas in varying proportions through the retorts was tried, and also the influence of the period of carbonisation at which the flow of diluting gas was started.

It was found that although the results obtained were far better than in the experiments made with the horizontal retorts, they were of the same kind, and that the gain in candle feet per ton rose gradually with increase in the volume of water gas used, reaching a maximum with about 40 volumes of water gas per 100 of coal gas, and decreasing when this point was passed.

Water Gas added per cent. of coal gas.	Candle feet per ton of coal.	Percentage gain per ton of coal in candle feet.
21·9	37,582	14·6
25·5	38,235	16·6
27·8	41,343	26·0
37·6	40,936	24·8
40·1	43,703	33·2
42·0	42,984	31·0
45·6	40,467	23·4

The most important data with regard to these experiments were given in a table at the end of a paper read before the International Engineering Congress at Glasgow, 1901, but the results are so full of interest that it is as well to give the full data for two experiments, in which 40 and 42 per cent. of water gas respectively were added, as it gives a better idea of the scale of the experiment :—

Coal used . . .	85·4 tons.	88 tons.
Total make (corrected) .	1,274,656 cub. ft.	1,294,946
Make per ton . .	14,925 cub. ft.	14,715

Illuminating power—		
(table photometer) .	14·4 candles	14·85
Total tar (hydraulic) .	690 gallons	651
Tar per ton . . .	8·07 „	7·4
Water gas added . .	42·0 per cent.	40·1
Water gas in mixture .	29·5	28·6
Water gas per ton of		
coal carbonised . .	4,415 cub. ft.	4,215
Candle feet per ton .	42,984	43,703
Standard for coal car-		
bonised alone . .	32,792	32,792
Increase in candle feet .	31·07 per cent.	33·2

Calorific Value—

	Gross.	Net.	Gross.	Net.
Calories . .	127·2	116·8	125·8	118·7
B.Th.U. . .	508·8	467·2	503·2	474·6
Carbon monoxide present				
in purified gas . .	14·0 per cent.		15·2 per cent.	
Gain in calorific value	25·5 „		22·4 „	

So that a gain of 31 to 33 per cent, in candle feet and 22 to 25 per cent. in total calorific value is attained.

This process was tried afterwards by Mr S. O. Stephenson at Tipton, who obtained very satisfactory results, whilst in 1905 Mr Brown, then of Nottingham, made an exhaustive series of tests with various classes of coals. Although he proved many advantages, the results were so erratic that its commercial value was far from demonstrated, and as far as I know nothing more has been done with it in this country.

One point, however, that shows the power of dilution by water gas in preventing degradation was that in the set used with water gas the scurf, *i.e.* deposited carbon, amounted only to 38·1 lbs. per mouthpiece per month, whilst with the set alongside using no water gas but the same coal and tenperature, the scurf amounted to 149·5 lbs. per mouthpiece per month.

With horizontal or inclined retorts the having to heat the water gas in an outside superheater is an insuperable objection, but the process I am now suggesting lends itself admirably to this purpose, as water gas blown into the coke just above the coke cooling and regenerator chamber would help to cool the lower part of the coke column, and by the time it reached the carbonising coal would be at the same temperature or even hotter than the tar vapour and gases leaving it, and would help in the fixation of the tar vapour, and also by dilution prevent degradation of hydrocarbons. There is very little doubt that, used in this way, 40 per cent. could be added without reducing the mixed gas below standard requirements, bringing the volume of mixed gases up to something approaching 17,000 cubic feet per ton of coal.

When speaking of ammonia, I reviewed Tervet's experiments in which, by passing hydrogen over red-hot coke at the end of the carbonising period, he was able to double and sometimes treble the yield of ammonium sulphate. In experiments he made with water gas he found this to act equally well; but the process was never adopted, as to obtain these results the coke heated in the retort had to be subjected to the gas for about three hours, which, of course, made it an impossibility, as the cost of fuel and water gas and the loss of the working capacity of the retorts far outweighed the advantages.

In the method I propose, however, three hours will about represent the time the coke would be subjected to the water gas in its passage from the carbonising top layers to the cooling chamber, and a large increase in the yield of ammonium sulphate should take place. The coke only being exposed to the maximum temperature for a very short time, and then being cooled slowly, should retain enough volatile matter to make a good domestic fuel, and diminution or absence of tar should raise its market price.

APPENDIX

WEIGHTS AND MEASURES

Avoirdupois Weight

Drachms.	Ounces.	Lbs.	Quarters.	Cwts.	Tons.	French Grammes.
1 =	·0625 =	·0039 =	·000139 =	·000035 =	·00000174 =	1·771846
16 =	1 =	·0265 =	·00223 =	·000558 =	·000028 =	28·34954
256 =	16 =	1 =	·0357 =	·00893 =	·000447 =	453·59
7,168 =	448 =	28 =	1 =	·25 =	·0125 =	12,700
28,672 =	1,792 =	112 =	41 =	1 =	·05 =	50,802
573,440 =	35,840 =	2240 =	80 =	20 =	1 =	1,016,048

Long Measure

Inches.	Feet.	Yards.	Fathoms.	Poles.	Furlongs.	Mile.	French Metres.
1 =	·083 =	·02778 =	·0139 =	·005 =	·000126 =	·0000158 =	·0254
12 =	1 =	·333 =	·1667 =	·0606 =	·00151 =	·0001894 =	·3048
36 =	3 =	1 =	·5 =	·182 =	·00454 =	·000568 =	·9144
72 =	6 =	2 =	1 =	·364 =	·0091 =	·001136 =	1·8287
198 =	$16\frac{1}{2}$ =	$5\frac{1}{2}$ =	$2\frac{3}{4}$ =	1 =	·025 =	·003125 =	5·0291
7,920 =	660 =	220 =	110 =	40 =	1 =	·125 =	201·16
63,360 =	5280 =	1760 =	880 =	320 =	8 =	1 =	1,609·315

Measure of Capacity

Pints.		Galls.		Cubic ft.		Litres.
1	=	·125	=	·02	=	·5676
8	=	1	=	·1604	=	4·541
16	=	2	=	·3208	=	9·082
64	=	8	=	1·283	=	36·32816
512	=	64	=	10·264	=	290·625
2560	=	320	=	51·319	=	1453·126
5120	=	640	=	102·64	=	2906·25

1 gallon	=	277¼ cub. in.
„	=	·16 cub. ft.
„	=	10 lbs. dist. water.
„	=	4·543458 litres.
1 cubic ft.	=	6·234 gallons.
1 grain	=	·064799 gram.
1 lb. avoir.	=	·453593 kilogram.
1 cubic metre	=	35·317 cu. ft.

Useful Data

1 lb. avoir. = 16 oz. = 7·000 grains = 453·59 grammes = 1·21527 lb. troy.

1 lb. troy =12 oz. = 5760 grains = 373·242 grammes = 0·82285704 lb. avoir.

1 oz. avoir. =437·5 grains=28·35 grammes=0·9114583 oz. troy.

1 cubic cent.=·06113 cub. in.=·282 fl. drms.=·00176 pint=·0352 fl. oz.

1 cubic foot = 28315·3 cc. = 6·2321 gallons = 28·3153 litres = 997·1364 fl. oz. = 49·8568 pints

1 gallon = ·16046 cub. ft. = 277·274 cub. in. = 4·54356 litres

1 cubic inch = 16·386 cc. = 0·577 fl. oz. = ·0164 litre = ·02885 pint.

1 litre = ·035316 cub. ft. = ·220096 gallon = 61·0270 cub. in. = 1·1761 pint.

1 fl. oz. = 28·396 cc. = 1·7329 cub. in.

1 pint = 567.919 cc. = ·020057 cub. ft. = 34·659 cub. in. = ·567920 litre.

1 gramme = ·002204 lb. = ·03527 oz. = 15·432348 grains.

Per cent. of tar × 2 = gallons per ton approximately.

1 per cent. nitrogen in fuel = 105 lbs. ammonium sulphate per ton (theoretical).

Conversion Factors

		Multiply by
To convert	grams into pounds avoirdupois .	0·002205
,,	kilograms into pounds avoirdupois	2·205
,,	pounds into grams . . .	453·6
,,	pounds into kilograms . .	0·4536
,,	litres into cubic metres . .	0·001
,,	litres into cubic feet . . .	0·0353
,,	cubic metres into cubic feet . .	35·315
,,	cubic feet into cubic metres . .	0·0283
,,	cubic feet into litres . . .	28·317
,,	cubic feet into gallons . . .	6·228

Table for Converting Degrees of the Centigrade Thermometer into Degrees of Fahrenheit's Scale

Centigrade	Fahrenheit	Centigrade	Fahrenheit	Centigrade	Fahrenheit
—90°	130°	40°	104°	170°	338°
85	121	45	113	175	348
80	112	50	122	180	356
75	103	55	131	185	365
70	94	60	140	190	374
65	85	65	149	195	383
60	76	70	158	200	392
55	67	75	167	205	401
50	58	80	176	210	410
45	49	85	185	215	419
40	40	90	194	220	428
35	31	95	203	225	437
30	22	100	212	230	446
25	13	105	221	235	455
20	—4	110	230	240	464
15	+5	115	239	245	473
10	14	120	248	250	482
—5	23	125	257	255	491
0	32	130	266	260	500
+5	41	135	275	265	509
10	50	140	284	270	518
15	59	145	293	275	527
20	68	150	302	280	536
25	77	155	311	285	545
30	86	160	320	290	554
35	95	165	329	295	563

$$\text{To convert °F to °C } \frac{(°\text{F} - 32) \times 5}{9} = °\text{C}$$

$$\text{To convert °C to °F } \frac{°\text{C} \times 9}{5} + 32° = °\text{F}$$

Table of the Corresponding Heights of the Barometer in Millimetres and English Inches

Millimetres.	=	English Inches.	Millimetres.	=	English Inches.	Millimetres.	=	English Inches.
720	=	28·347	739	=	29·095	758	=	29·843
721	=	28·386	740	=	29·134	759	=	29·882
722	=	28·425	741	=	29·174	760	=	29·922
723	=	28·465	742	=	29·213	761	=	29·961
724	=	28·504	743	=	29·252	762	=	30·000
725	=	28·543	744	=	29·292	763	=	30·039
726	=	28·583	745	=	29·331	764	=	30·079
727	=	28·622	746	=	29·370	765	=	30·118
728	=	28·662	747	=	29·410	766	=	30·158
729	=	28·701	748	=	29·449	767	=	30·197
730	=	28·740	749	=	29·488	768	=	30·236
731	=	28·780	750	=	29·528	769	=	30·276
732	=	28·819	751	=	29·567	770	=	30·315
733	=	28·858	752	=	29·606	771	=	30·355
734	=	28·898	753	=	29·645	772	=	30·394
735	=	28·937	754	=	29·685	773	=	30·433
736	=	28·976	755	=	29·724	774	=	30·473
737	=	29·016	756	=	29·764	775	=	30·512
738	=	29·055	757	=	29·803			

Thermal Data

The British Thermal Unit is the amount of heat required to raise 1 lb. of pure water 1° F., or from 39·1° F. to 40·1° F.

The Large Calorie (French Unit) is the amount required to raise one kilogram of water through 1° C.

The Small Calorie (Scientific Unit) is the amount of heat required to raise 1 gramme of water from 0° C. to 1° C.

The Pound Centigrade Unit is the amount of heat required to raise 1 lb. of water from 0° C. to 1° C.

B.T.U.		Ca.		Ca.		Lb. C.U.		Foot-lbs.
1	=	0·252	=	252	=	0·555	=	776
3·9682	=	1	=	1·000	=	2·2046	=	3080
0·003968	=	0·001	=	1	=	0·002046	=	3·08
1.8	=	0·4536	=	453·6	=	1	=	1397

Weight and Volume of Gases

	Weight.		Volume.	
	Per Cubic Metre in Kilos.	Per Cubic Foot in Pounds.	Per Kilo. in Cubic Metres.	Per Pound in Cubic Feet.
Air . .	1·29318	0·08073	0·773	12·385
Nitrogen .	1·25616	0·07845	0·796	12·763
Oxygen . .	1·4298	0·08926	0·699	11·203
Hydrogen .	0·08961	0·00559	11·160	178·83
Carbon dioxide	1·9666	0·12344	0·508	8·147
Carbon monoxide	1·2515	0·07817	0·800	12·800
Carbon vapour	1·0727	0·06696	0·932	14·930
Aqueous vapour	0·8047	0·05022	1·242	19·912
Sulphurous acid	2·8605	0·1787	0·349	5·596
Ethylene .	1·2519	0·07814	0·799	12·797
Methane . .	0·7155	0·04466	1·397	22·391
Acetylene .	1·1900	0·07428	0·840	13·456
Benzol . .	3·3333	0·208	0·303	4·808
Ethane . .	1·3415	0·08565	0·746	11·950

Thermal Value of Gaseous Fuels.
Per Cubic Foot and Per Pound.

	Cubic Feet per Pound at 60° F.	British Thermal Units.	
		Per Cubic Foot gross.	Per Pound.
Coal gas (16 c.-p.) .	31	620	19,220
,, (14 c.-p.) .	32	540	17,280
Water gas . .	26·6	300	7,980
Mond gas . . .	16·4	154	2,525
Dowson gas . .	15·9	148	2,353
Suction plant gas .	16	135	2,160

Average Thermal Value of Fuels per Pound.

	Calories.	British Thermal Units.
Coal—		
Newcastle . . .	8,446	15,203
Welsh	8,402	15,123
Lancashire . . .	8,113	14,602
Derbyshire . . .	8,120	14,616
Anthracite . . .	8,677	15,619
Coke—		
Oven coke . . .	8,020	14,436
Gas coke	7,900	14,226
Peat—		
30 per cent. water . .	3,000	5,400
20 ,, ,, . .	4,000	7,200
10 ,, ,, . .	5,000	9,000
5 ,, ,, . .	5,500	9,900

	Calories.	British Thermal Units.
Wood—		
Ash	4,711	8,480
Beech	4,774	8,591
Birch	4,771	8,586
Elm	4,728	8,510
Fir	5,035	9,063
Oak	4,620	8,316
Pine	5,085	9,153
Charcoal	8,137	14,646

Liquid Fuels

Petroleum (fuel)—		
American	10,904	19,627
Russian	10,800	19,440
Texas	10,700	19,242
Caucasus	10,340	18,611
Borneo	10,461	18,831
Burmah	10,480	18,864
Petroleum spirit (·684)	11,624	20,923
Shale oil	10,120	18,217
Blast furnace oil	8,933	16,080
Heavy tar oil	8,916	16,050
Alcohol absolute	7,184	12,931
,, 10 per cent. water	6,400	11,520
,, 20 ,, ,,	5,700	10,260
,, methylated	6,200	11,160

Gaseous Fuels

	Calories.	British Thermal Units.
Natural gas	12,008	21,615
Coal gas (London, 16 c.-p.) .	10,666	19,220
Water gas	4,430	7,980
Mond gas	1,402	2,525
Dowson gas	1,310	2,353
Suction-plant gas . . .	1,200	2,160
Air-coke gas	540	972
Blast-furnace gas . . .	528	951

INDEX

Absorptive power of coal, 26
Action of solvents on coal, 27
Actions in a coal fire, 231
American coke oven, 103
Ammonia, fixed, 266
  formation of, 259
  free, 266
  in coal gas, 255
  yield of, 259
Ammonium sulphate, 246, 267
Analyses of coal ash, 223
Anilin, 30, 187
Anthracene oil, 188
Appolt oven, 106
Assimilation of carbon dioxide, etc., 4
Atmosphere, changes in, 2
Autocarburetting, 147, 293

Beehive coke, 224
  ovens, 101
Benzenoid tars, 203
Bituminous coal, 39
Black heads, 226
Blass' experiments, 147
Blast furnace liquor, 225
  tar, 205
Boghead cannel, 17
Bornstein, 153, 160
British Thermal units, 4
Brown coals, 40
Burgess & Wheeler, 167, 214
Bury on coke oven gas, 113

Calories, 4
Calorific value of coal, 52
  coal constituents, 53
Carbon dioxide, 23
Carbolic acid, 188
Cauliflower heads, 225
Cellulose, 10
Chamber carbonisation, 91
Charco, 241
Chlorophyll, 3
Classification of coals, 35
Coal, absorptive power of, 26
  ash analyses, 223
  brown, 40
  charges, 9
  coking power of, 210
  composition of, 47
  consumption, 60
  decomposition of, 116
  distillation of, 160
  economy in use of, 62
  fields, origin of, 67
  fires and smoke, 231
  ignition point of, 22
  mineral constituents of, 12
  pyrites in, 21
  resin constituents in, 16
  retorts, 65
  swelling of, 143
  weathering of, 20
Coalexld, 240
Coalite, 239
Coke, 208
  binding material in, 12, 217
  effect of temperature on, 224
  fires, 236
Coke fracture of 140,
  from horizontals, 242
  from verticals, 242
  gas, 229
  hairs, 217
  high temperature, 229
  low temperature, 215, 238
  meiler, 101
  metallurgical, 228
  ovens, 105
    American, 103
    Appolt, 106
    beehive, 101
    Coppée, 106
    Otto, 107
    Simon-Carvès, 106
  oven gas, 108
  oven liquor, 264
  tar, 204
  temperature of formation of, 213
Coking, causes of, 218
Coking power of coals, 210
Composition of coal, 47
  gas liquor, 262

Composition of coal—*continued.*
lignites, 49
peat, 49
tar, 186
Conduction of heat through retort, 125
Constam and Kolbe, 119, 159, 175
Continuous carbonisation, 292
Cyanogen, 269

Decomposition of resin compounds, 17
Degradation of gas by temperature, 88
Dessau vertical retort, 75
Destructive distillation, 116
Dinsmore process, 199
Distillation, 116
coal, 160
lignite, 158
peat, 156
wood, 150
Disulphide of iron, 273
Drift deposits, 7
Droylsden installation of verticals, 88

Economy of coal, 62
Effect of temperature in carbonisation, 163, 280
Endothermic compounds, 117
Endothermicity of coal, 117
Energy, sources of, 1
English coal fields, 57
Ethylene series, 184
Euchêne, 118, 156, 177
Exothermic compounds, 117

Ferrocyanides, 270
Fireclay retorts, 70
Fixed ammonia, 266
Formation of boghead cannel, 17
coke, 213
vegetable deposits, 67
Fracture of coke, 140
Free ammonia, 266
Fully charged retorts, 96, 136

Gas coke, 229,
from vertical retorts, 280
liquor, 262
low temperature, 164
Gasification of tar, 196
Glover's chamber retorts, 98, 140
Glover-West system, 85
Gruner's classification of coal, 36

Heat conductivity of refractory materials, 129
in a retort, 130
Heat utilisation in carbonisation, 122
Hexahydrides, 185
High temperature gas, 277
Horizontal retorts, fully charged, 97
Humic acid, 13
Humus, calorific value of, 54
Hydrocarbons, 182
Hydrocyanic acid, 268
Hygroscopic water, 218

Ignition point of coal, 22
Illuminating power, 285
Isolation of resin compounds, 17
Isomerism, 185

Klönne chamber ovens, 96

La Villette experiments, 172
Leakage in clay retorts, 70
Lignites, 40
composition of, 49
distillation of, 158
Ligno-cellulose, 10
Lignose, 12
Liming of coal, 261
Liquor, blast furnace, 265
coke oven, 264
gas, 262
London Argand, 287
Low temperature coke, 215
gas, 164, 276
tar, 191

Mahler, 119
Meiler coke, 101
Metallurgical coke, 228
Metamerism, 185
Methane-hydrogen, 207
Metropolitan Argand, 287
Microscopical character of coal, 37
Mineral constituents in coal, 12
Murdoch's experiments, 64

Naphthalene, 187
Naphthenes, 185
Nitrates, 246
Nitrobenzene, 187
Nitrogen in bituminous shales, 251
coal, 248

Nitrogen in—*continued*.
coke, 250
peat, 247
tar, 250
vegetation, 245

Oven, American, 103
beehive, 101
coke, 224
recovery, 106
Oxygen in tar, 189

Paraffinoid tars, 203
Paraffin series, 183
Peat, composition of, 49
distillation of, 155
Phenoloid tar, 207
Pit water, 218
Polymerism, 185
Porter and Ovitz, 164
Primary products of distillation, 275
Proposed classification of coals, 45
Pyridine, action on coal, 30
Pyrites in coal, 21, 273

Ratio of the constituents in coal, 47
Recovery ovens, 106
Refractory materials, heat conductivity of, 129
Resin constituents in coal, 16
decomposition of, 17
isolation of, 17
Retorts, Clegg, 68
fireclay, 70
heating, 126
Murdoch, 65
scurfing, 71
vertical, 73

Ste Claire Deville, 137, 172, 189
Saturated hydrocarbons, 182, 189
Scurfing retorts, 71
Secondary reactions, 170
Semet-Solvay tar, 205
Semi-chamber retorts, 140
Settle-Padfield retort, 289
Shale, formation of, 17
Shipment of coal, 21
Simon-Carvès tar, 204
Size of coal in carbonising, 139
Smoke, production of, 230
Smokeless fuels, 240
Splint coal, 206
Spontaneous ignition, 22
Sulphate of ammonium, 267
Sulphocyanides, 270
Sulphuretted hydrogen, 274
Sulphur in coal, 271
Sun, energy due to, 3
Swelling of coal, 143

Tar, 180
benzenoid, 203
blast furnace, 205
coke oven, 204
composition of, 186
distillation, 187
effects of temperature on, 190
from vertical retorts, 195
gasification of, 199
high temperature, 196
low temperature, 191
oxygen in, 189
paraffinoid, 203
phenoloid, 207
water gas, 207

Temperature of coal in retort, 132
gas on carbonisation, 144
retort charge, 138
Thiophene, 274
Travel of gas in retort, 137
Tubes, carbonisation in, 140
Tully's methane-hydrogen, 201

Ulmic acid, 13
Unsaturated hydrocarbons, 183
Utilisation of heat in carbonisation, 122

Vapourisation, 116
Vegetable deposits, 5
Vegetation, 5
Vertical retorts, 73

Water from carbonisation, 262
in coal, 34
gas in carbonisation, use of, 146, 293
tar, 207
Weathering of coal, 20
White Park and Dunkerley, 166
Wood distillation, 150
Woodall-Duckham retort, 80
Wright, L. T., 171, 193

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